Whey Permeate Fouling of Evaporators

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Abstract

Whey permeate fouling was studied to gain a better understanding of the processes involved and find methods of alleviation. An apparatus was built which allowed study of fouling under industrial conditions.

It was found that pretreatment by heating at 80°C for two minutes and then centrifuging at 630 g reduced fouling in the apparatus by 94%. This was attributed to precipitation of calcium phosphate in the solution bulk during preheating, which reduced the level of supersaturation. Heat treatment with the same conditions but without centrifuging reduced fouling by only 39%. Precipitate which forms in the bulk of solution fouls in later heat treatment processes and separation of the precipitated mineral is needed to minimise fouling.

Storage time affected fouling. In the short term (about 2 weeks), fouling slightly increased with storage time. When held for longer times (about 1 month) whey permeate did not appreciably foul.

The use of additives was also found to be an effective alleviation method, reducing fouling by 66% with 0.1% addition (by dry weight) of tetrasodium pyrophosphate. This addition would increase the price of a ton of lactose by $16.32 /ton.

Nanofiltration, ion dialysis and electrodialysis were also examined, but rejected as being uneconomic.

By observing the effect of preheating and storage time it was proposed that calcium phosphate exists in whey in two forms. The majority of the minerals are associated with non-protein nitrogen (NPN) species, which tends to provide stability and prevent precipitation. In the other form the calcium phosphate is in solution as free ions. When the NPN species release minerals due to cleavage by enzymes or denaturation by heat, the concentration of ionic species increases past the solubility product and precipitation occurs.

Acknowledgments

First of all I would like to thank Dr Ken Morison for his supervision of this research. Ken was always willing to listen to my ideas and respond with his, and always had a solution when it appeared the project might get stuck.

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Last but not least I thank my parents for listening to me during my fortnightly telephone calls home, especially my father for giving me encouragement to keep going and actually understanding what I was talking about.

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Symbols

A	m^2	Area
C_d	-	Coefficient of discharge
D	m	Diameter
g	$m\ s^{-2}$	Gravity
K_{sp}	$mol\ L^{-1}$	Solubility product
L	m	Length
Q	$J\ s^{-1}$	Rate of heat transfer
R_T	$m^2\ K\ W^{-1}$	Total thermal resistance
T_i	K	Temperature at point i
U	$W\ m^{-2}\ K^{-1}$	Overall heat transfer coefficient
U_D	$W\ m^{-2}\ K^{-1}$	Overall heat transfer coefficient when dirty
f	-	Fanning friction factor
$h_{i,j}$	$kJ\ kg^{-1}$	Enthalpy of phase i at condition j
k_i	-	Student-t distribution at i
n	-	Sample size
r	m^2	Radius
s	-	Standard deviation of a sample of a population
v	$m\ s^{-1}$	Velocity
x_i	m	Thickness of section i
α	$W\ m^{-2}\ K^{-1}$	Heat transfer coefficient
γ_i	-	Activity coefficient of species with a valency of i
ΔT_{lm}	K	Log mean temperature difference
ΔP	Pa	Pressure drop
θ_i	K	Temperature at point i.
λ	$W\ m^{-1}\ K^{-1}$	Thermal conductivity
ρ	$kg\ m^{-3}$	Density

1 General Introduction

The aim of this research was to gain a better understanding of whey permeate fouling in evaporators, and from this devise methods to alleviate the problem.

Whey permeate is a byproduct from whey protein concentrate (WPC) manufacture. It is estimated that in the 1997/98 season, 5.3 billion litres of milk were produced in New Zealand, resulting in about 2.4 billion litres of whey. About 1.5 billion litres of this was used to make lactose at Lactose New Zealand's (LNZ) Kapuni site (Kellam, 1998).

Lactose production is a relatively complex dairy process (section 3.2). The first step is to increase the total solids by evaporation from 12% to ~45%. During this process, heavy fouling occurs on the walls of the evaporator tubes, which reduces efficiency and limits run times. During cleaning, large chunks of the deposit flake off and settle on the distribution plate of the following effect, preventing total cleaning of all tubes.

The problem has two main causes. The most important is that whey permeate contains large amounts of calcium phosphate, a reverse solubility salt. As the feed is heated, the calcium phosphate becomes supersaturated and precipitates onto the evaporator walls. The second, and less understood factor, is the importance of small proteins in whey permeate. Although the feed has been through the WPC process which removes as much of the whey proteins as possible, non-protein nitrogen (NPN) sources still remain. This NPN is made up of urea, protein fragments, peptides and vitamins which are still present in whey permeate after WPC processing. These components play an important role in the fouling process. They tend to stabilise calcium phosphate in solution before heating, and denature during heating to form part of the fouling layer (section 6.7).

Since whey permeate is not an internationally significant product, literature on its fouling is quite limited. Literature on milk and WPC fouling is extensive however (section 2.2), and many of the same concepts apply. Previous attempts to alleviate whey permeate fouling have centred on better cleaning methods, rather than preventing the problem from occurring. This research looked at understanding the mechanism by which fouling occurred (section 2.3), and the involvement of calcium phosphate in this process (section 2.4). This allowed several methods of demineralisation to be proposed (section 3.4).

2 Introduction to Fouling

Fouling is the formation of unwanted solid deposits within process plants, and is the major limiting factor in continuous food processing (Fryer & Belmar-Beiny, 1991). It is extremely undesirable for several reasons, the most important being the resistance to heat transfer it produces, and the downtime required for cleaning.

Extra heat resistance is a concern in processing plants as it acts as an insulator and decreases the overall heat transfer coefficient. To overcome this there are several options. If the problem is being looked at in the design stage, the heat transfer area can be increased. If the problem is encountered during processing, fouling can be counteracted by lowering the flow rate. This is not often practiced as lower flow rates cause more fouling. It is more common to increase the temperature difference between the product and heating medium.

Consider a falling film evaporator that processes whey permeate. A totally clean evaporator may be able to process 40,000 L/hr of whey permeate. By the end of a run, perhaps only 32,000 L/hr can be processed and give the same product. This has two effects. Firstly, at the end of the run the reduced flow rate must still be spread over the same area. This causes problems for the evaporator distribution devices which spread this smaller flow over the same size heat transfer area. This increases the chances of 'dry-on' (when an evaporator tube becomes totally dry) which causes significant fouling and may cause blocked tubes. Secondly, designers must take the reduced overall heat transfer coefficient into account. This means providing more heat transfer area, which increases capital costs.

Fouling also increases that temperature difference required between product and the heating medium (usually steam). This raises energy costs in multi-effect evaporators, as the amount of vapour recompression required increases.

The most obvious problem with fouling is the increased downtime, as plants which foul cannot be run as long between cleanings. This is clear in the difference between petroleum plants which can run for years without cleaning (Crittenden *et al.*, 1992), whereas a typical dairy processing unit operation might run for 8-12 hours (Fryer & Belmar-Beiny, 1991; Delplace *et al.*, 1994) (Table 2.1).

Table 2.1 *Typical run times before cleaning for unit operations in the dairy industry*

Equipment	Run time before cleaning
Centrifuge	8-12 hrs
Pasteuriser	8-12 hrs
Evaporator	10-14 hrs
Spray Drier	5-6 weeks

Fouling also increases the length of the cleaning cycle and the volume of chemicals needed to ensure high hygiene levels. Generally the downtime required to clean an evaporator is two hours, but can be as long as four hours (Woodshead, 1997). If the amount of deposit is severe, large amounts of physical work may be required to inspect and clean equipment. This extends downtime and more importantly increases cleaning costs.

Fouling may lead to problems with product quality as it is a dynamic process. Fouling resistance is zero at startup if cleaning has been successful, and builds over time. This means that the process variables will have to be continuously changed to produce a constant product, and control devices may be placed under stress to achieve this. Foulant can also break off and find its way into the final product. This gives rise to non-specification production.

Even small amounts of fouling provides crevices and stagnant areas for bacteria growth to occur. This is important for processes where the product's hygiene and safety must be guaranteed, e.g., all dairy processes.

The dairy industry has partially solved the fouling problem by devising very efficient cleaning methods such as CIP (Cleaning In Place). The extra equipment and piping needed for this adds to capital and maintenance costs. Fryer *et al.* (1995) also mention lost opportunities as a cost of fouling. High viscosity, high fouling food materials such as whipped cream and margarine sometimes require special heat transfer equipment (i.e., scrapped surface heat exchangers) to be processed. This raises production costs and makes some products commercially unviable.

2.1 Basic Theory

Fouling has been described as "the major unresolved problem in heat transfer" (Taborek *et al.*, 1972). Whereas other aspects of heat transfer have been extensively studied (e.g., fluid mechanics) fouling has had nowhere near as much research performed on it. This may be because it is a difficult subject to handle, due to its kinetic nature, numerous mechanisms and especially the strong dependence on the fluid being processed. Most of the research on fouling has been empirical in nature.

In the past little thought has been given to fouling data. Generally, the overall heat transfer coefficient (U) is used to design heat transfer equipment (Eqn. 1.1).

$$Q = UA\Delta T_{lm} \tag{1.1}$$

In this method, U describes the combination of resistances seen in figure 2.1

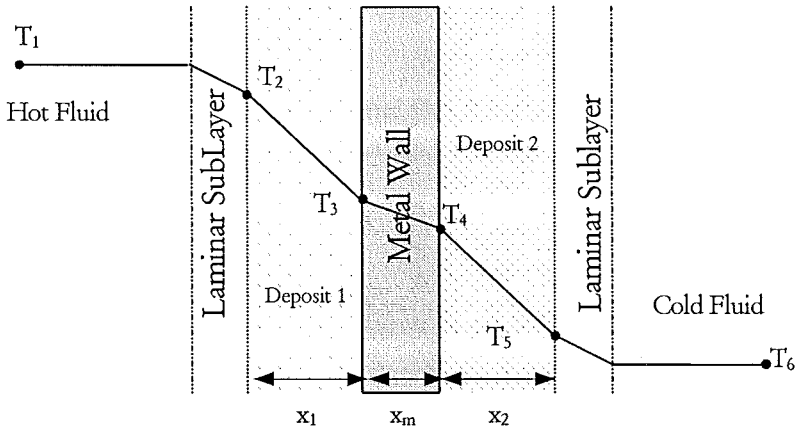

Figure 2.1 *Resistance to heat transfer from deposits and metal (Bott, 1995)*

Fouling deposits act as insulators. They increase the distance that heat must be conducted, and have thermal conductivities far lower than metals (table 2.2).

Table 2.2 *Thermal conductivities of selected foulants and metals (Bott, 1995; Incropera & De Witt, 1990)*

Material	Thermal Conductivity (W/m.K)
Biofilm	0.6
Calcium sulphate	0.74
Calcium carbonate	2.19
Copper	400
Mild Steel	27.6
Stainless Steel	15

The resistance to heat flow across a solid surface is defined as

$$R = \frac{x}{\lambda} \tag{1.2}$$

where x is the solid thickness and λ is the thermal conductivity. The heat transfer must pass through each section of insulation. By referring to figure 2.1, the heat balance can be written as in equation 1.3.

$$q = \frac{T_2 - T_3}{\left(\frac{x_1}{\lambda_1}\right)} = \frac{T_3 - T_4}{\left(\frac{x_m}{\lambda_m}\right)} = \frac{T_4 - T_5}{\left(\frac{x_2}{\lambda_2}\right)} \tag{1.3}$$

Also

$$q = \alpha_1(T_1 - T_2) = \alpha_2(T_5 - T_6) \tag{1.4}$$

where α_1 and α_2 are the heat transfer coefficients for the hot and cold fluids respectively.

These individual resistances can be summed to form the total thermal resistance, R_T.

$$\frac{1}{U} = R_T = \left(\frac{x_1}{\lambda_1}\right) + \left(\frac{x_2}{\lambda_2}\right) + \frac{x_m}{\lambda_m} + \frac{1}{\alpha_1} + \frac{1}{\alpha_2} \tag{1.5}$$

Therefore the rate of heat transfer can be expressed as

$$Q = \frac{A(T_1 - T_6)}{R_T} \tag{1.6}$$

where A is the heat transfer area.

The thickness of deposit (x) cannot be evaluated in most situations, so the designer has two choices. They can designate the fouling resistance as shown in equation 1.7.

$$U_D = \frac{1}{R_T} \tag{1.7}$$

where R_T is empirically obtained and presented as shown table 2.3.

Table 2.3 *Fouling resistances in water systems (Bott, 1995)*

Fluid Type	Total Fouling Resistance (R_T) (10^4 m^2K/W)
Sea Water	1.75 - 3.5
River Water	3.5 - 5.3
Treated Boiler Feedwater	0.9

This information is purely empirical and neglects to take into account the fouling conditions, e.g., hydrodynamics, temperature differences. Therefore the data is of little use, especially when it is considered that this sort of information for dairy fluids is practically non-existent.

The second method (Bott, 1995) uses the fact that at steady state and fouled conditions:

$$q = U_D(T_1 - T_6) \tag{1.8}$$

Where U_D is the overall heat transfer coefficient when the equipment is 'dirty'. U_D can some times be found in data tables, such as those published by the Tubular Exchanger Manufacturers Association (TEMA, 1968), but only for special applications. Again, it is not often specified as to what conditions this data applies. This method is not appropriate for dairy applications, because equipment must be cleaned before the level where fouling (and U_D) becomes constant. In fact, fouling is a kinetic process as shown in figure 2.2

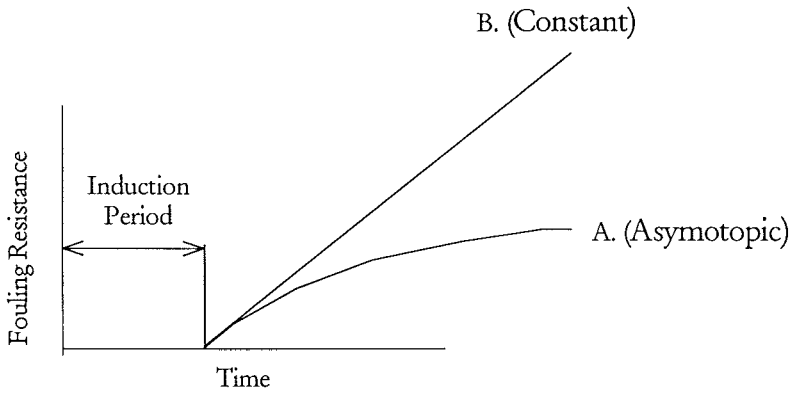

Figure 2.2 *Fouling resistance as a function of time (after Taborek 1972)*

The fouling resistance when the plant starts up will be zero, assuming it has been properly cleaned. For some plants, e.g., petroleum processors, the fouling resistance will then go through a period of no or very little increase. This induction period is so small for most dairy heat transfer operations that it can be considered negligible (150 seconds for whey at 96°C, Belmar-Beiny & Fryer, 1992). The next phase consists of a steady increase of resistance until an asymptote is reached (curve A). Although this asymptote may exist in theory, it is of no use in general processing. Usually a point is reached where no more product may be treated until the equipment is cleaned. This point is when the equipment can no longer provide the necessary temperature difference to keep the outflowing product within the required specification. This occurs when the fouling is still within its constant rate period (line B).

Fouling resistances are usually estimated at the point of cleaning. This means the equipment's surface area will be large enough to process product correctly right up to the point of stoppage. This area is often much bigger than it needs to be, and often leads to 'self-fulfilling prophecies', as startup conditions can be considerably different (Schreier & Fryer, 1995). Designing with larger fouling resistances than necessary does not necessarily give longer run times (Kearn & Seaton, 1959). Consider a heat exchanger which begins a run totally clean, it is designed to operate when heavily fouled so initially the temperature difference or surface area is much larger than it needs to be. This means that the product is heated to greater temperature and fouls quicker than it otherwise would have.

Since an understanding of fouling is so important in design, it is surprising that it has been given so little attention by most authors. When discussing fouling in evaporators, Billet (1989) admits that:

> *"In practice the overall coefficient of heat transfer frequently can not be derived mathematically... this is because the equations apply only under the assumption that thermal resistance is not increased, i.e., that heat transfer is not impaired by scaling... "*
> *(Billet, 1989)*

Although noting this, Billet does not acknowledge any further method of estimating the fouling resistance.

Bolt (1995) talks extensively about fouling of heat exchangers. He mentions that "the problems associated with heat exchanger fouling have been known since the first heat exchanger was invented". Later he notes that "at best the tables of fouling resistances give a range of mean fouling resistances, but in general there is no information on the conditions at which these values apply."

In industrial situations, heat transfer equipment is usually designed by equipment suppliers who use their own information in the design process. The fouling values they use are produced from a large body of empirical experience that they can draw on.

2.2 Dairy Fouling

A large amount of literature has been written on dairy mineral fouling. Bell and Saunders (1944) first reported the problem with respect to ultra-heat treatment (UHT) plants, but did little experimental work. Burton (1968) reviewed the problem, and noted that fouling in UHT plants could generally be classified into two types (figure 2.3). He classified the curdy, soft material formed at low heat exchanger temperatures as type A. It contains about 60% protein and 35% minerals with the remainder being fat (Burton, 1988). The protein is mainly β-lactoglobulin, which makes up only 10% of raw milk protein (Lalande *et al.*, 1985; Tissier & Lalande, 1986a). Type B fouling material was classified as hard and brittle, and is mainly formed by mineral deposition (Lyster, 1965). Calcium is the most significant component in this deposit (Grandison, 1996). The fouling that occurs in the evaporation stage of lactose production is type B fouling. However differences occur because UHT plants subject product to much higher temperatures.

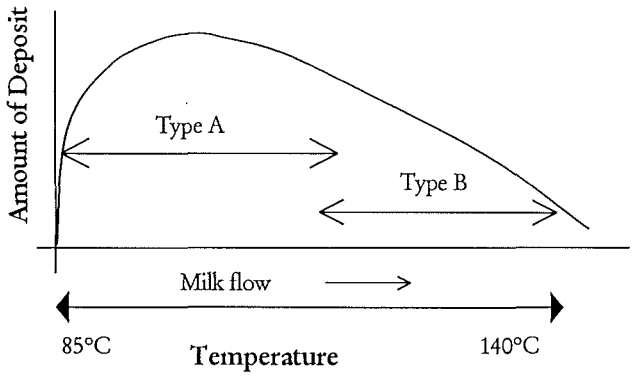

Figure 2.3 *Variation of deposit type with temperature along flow path*

Burton (1968) also showed that preheating milk at 95°C for 15 seconds significantly reduced fouling in UHT (ultra-heat treated) milk production. It was proposed that this treatment denatured the soluble proteins that were present, which were then less able to foul in the UHT process. This meant the nature of the deposit changed, with less proteinacous 'type A' fouling occurring, and more mineral based 'type B' fouling being deposited. It was also noted that after preheating, parts of the UHT plant upstream actually fouled more. Burton (1968) attempted to explain this by stating:

"... it is curious that there is normally much more of this deposit [type B] at the high temperature end of the heating section than if preholding is not used. It is as if the precipitation of the type A deposit [when no preheating has been used] at an early stage [in the UHT plant] removes some of the potential type B deposit which would otherwise be precipitated at a high temperature."
(Burton, 1968)

This explanation seems unlikely. Burton is suggesting that in the section where untreated milk gives type A deposit, the loss of protein stabilisation causes some minerals to precipitate as well. This is reasonable since proteins assist in mineral stability (especially casein). However, this would not account for the behaviour above. In the heat-treated milk, any minerals that would have been lost due to heat destabilisation would be precipitated in the preheat, or precipitate earlier in the UHT plant. Therefore, this theory fails to account for the extra mineral fouling that occurs at the end of the UHT. It is likely that the preheating precipitates minerals while in the holding section, which later bond onto UHT equipment (this was observed in this study, section 5.1.6). It is difficult to account for the extra fouling occurring in the last section of the UHT. It may be that the milk was not cooled after its heat treatment, and therefore entered the UHT at a higher temperature. This would mean the milk would reach a greater temperature during processing and therefore precipitate more minerals than it would otherwise. Since temperatures and final concentrations were not reported in Burton's work, this seems possible.

Burton (1968) also showed that mineral fouling occurred below temperatures normally associated with type B fouling. It was noticed that even where type A fouling was predominant, it was attached to a 'filmy clear deposit which covers the entire heating surface'. This finding was confirmed in this research (section 5.1.6). The clear film was found to be 53% ash, 46% protein, which is a much higher mineral content than is found in type A fouling.

The effect of storage time was also covered in the same research (Burton, 1968) (figure 2.4).

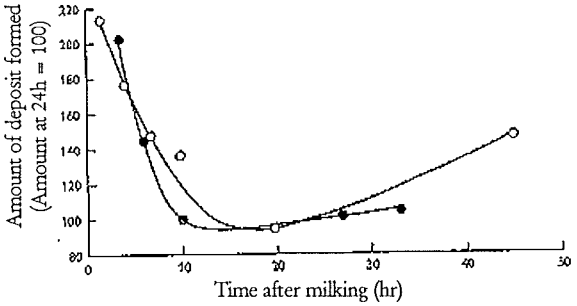

Figure 2.4 *Effect of refrigerated storage time on fouling (Burton, 1968)*

It was noted that fouling dropped quickly with refrigerated storage time up to ~24 hours, then rose slightly. Burton was unable to explain this, but suggested that:

> *"... it may be caused by redistribution of some of the mineral components following the drop in temperature when the milk leaves the udder, or it may be caused by the disappearance of some minor protein component on ageing."*
> *(Burton, 1968)*

It is hard to apply this vague explanation to what is observed above. The behaviour of milk is not that different to whey permeate (section 5.1.4) when the first 10 hours is neglected. Figure 2.4 shows that after this time, storage time increases fouling. This may be due to the proteins supporting the casein micelle being cleaved by the action of enzymes. This releases minerals into the solution phase of the milk system, and increases supersaturation. This mechanism is proposed as the reason that whey permeate fouling increases after a few days of storage (section 6.3). The initially high deposits observed in milk fouling may be due to other factors, such as aeration of the milk which would increase fouling (Walstra & Jenness, 1984).

The next major review of dairy mineral fouling was performed by Hobman (1984). At the time, deproteinated milk serum (DMS) or whey permeate, was a newly created by-product from whey protein concentrate (WPC). Uses for this were discussed. It was noted that since whey permeate is virtually saturated with calcium (Nickerson, 1979), concentration by evaporation would lead to rapid scaling. It was mentioned that the reverse solubility curve of calcium phosphate aggravates this problem (Brule *et al*, 1978; Summers & Okos, 1982). Hobman (1984) also claimed that the precipitated minerals would become an impurity not easily removed by washing (Nickerson, 1979). Pretreatment was emphasised as being necessary with a DMS feedstock to control the fouling problem (Landre, 1975; Nicolaisen, 1975).

The suggested pretreatments were:

- reducing pH to prevent formation of insoluble salts

(Nickerson, 1979)

- addition of chelating agents

(Evans & Young, 1982; Evans *et al.*, 1982)

- removal by concentration and heat treatment

(Pederson, 1980).

Hobman went on to describe a pH and heat treatment process, which removed precipitated calcium phosphate by centrifuging (Hobman & Robinson, 1980). This is described in section 3.4.

Since fouling in evaporators is mainly 'type B' fouling, calcium phosphate is the main contributor to this fouling. The precipitation mechanism by which this occurs is discussed in section 2.4.1. It has been proven that increasing calcium content in a dairy fluid increases fouling (Delsing & Hiddink, 1983).

The effect of surface finish has also been researched. It was found that using a teflon coated tube provided no reduction in fouling compared to a traditional 304 stainless steel surface (Yoon & Lund, 1989).

2.3 The Mechanisms of Fouling

Burton (1968) proposes a mechanism for dairy fouling where deposit formation is considered as two separate processes. First, the high temperature conditions cause some milk components to become supersaturated. Secondly, these components will precipitate on a surface if available, or otherwise in the bulk. If the components aggregate in the bulk it was proposed that they will not be available to adhere later in the process. This was not found to be true in this research (section 5.1.6).

When a heating process is run at steady state, the temperature distribution can be shown as in figure 2.5.

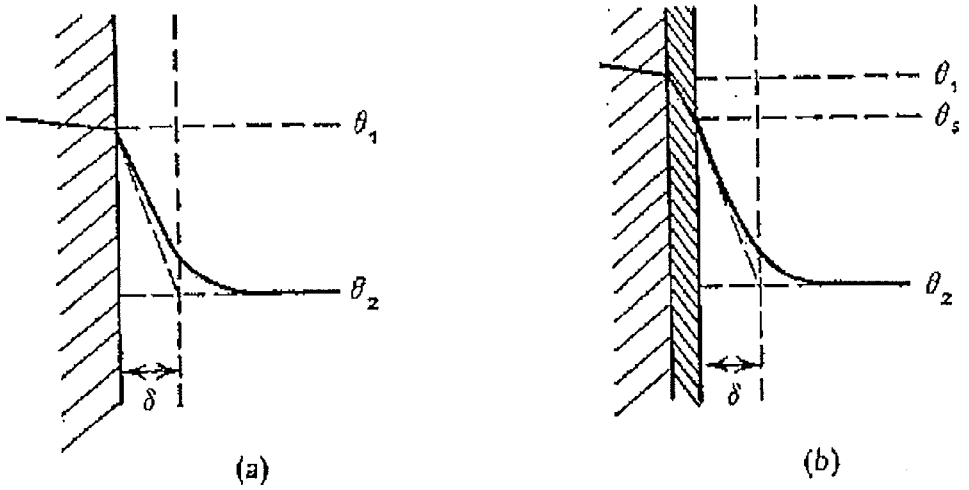

Figure 2.5 *Temperature distribution at a heating surface (Burton, 1968)*

In figure 2.5a the temperature of the bulk liquid is θ_2, and the temperature at the wall is θ_1. When the fluid flows under turbulent conditions, as in an evaporator when a large vapour core is present, the temperature profile between θ_1 and θ_2 is almost linear for a section of thickness δ.

The liquid temperature is highest close to the wall, and therefore the highest level of supersaturation of inverse solubility salts occurs there (Davies *et al.*, 1997). The surface also provides a suitable site for the formation of nuclei and deposit builds up as shown in figure 2.5b.

Burton (1968) forwards the theory that in a preheater with very low velocity conditions, only a small volume of milk/whey permeate will be available to become supersaturated. Once the fluid surrounding the wall has deposited all of its minerals, deposition will be mass transfer controlled rather than reaction (crystallisation) rate controlled. Precipitation will then occur in the bulk of the solution, and the precipitate will not be free to foul later. These conditions would be hard to create in an industrial process where a continuous operation is required and would have an extremely low thermal efficiency. Also, convectional currents will ensure that there is always some level of mixing.

Bott (1995) gives a very though account of crystallisation fouling, which visualises the process as occurring in three stages:

- Supersaturation of the solution occurs.
- Formation of crystal nuclei and crystallites.
- Growth of crystals.

In the processing of whey permeate, supersaturation has occurred before the product even enters the evaporator. The second stage must occur before crystals can grow. Crystals are only stable in groupings above a certain critical number, below this number they tend to redissolve. A grouping with less than the critical number of members is called a nuclei. Nuclei formation is catalysed by impurities or surfaces. In heat exchange equipment the heat transfer surface provides an abundant source of nucleation sites.

The mechanism described above is referred to as heterogenous nucleation, and is the process that commonly occurs in industrial situations. Homogenous nucleation occurs when no impurities and surfaces are present. This mechanism requires extensive supersaturation and proceeds by nuclei spontaneously forming in the bulk. Smith (1993) gives an excellent summary of these processes.

Crystal growth occurs once stable nuclei have been formed. Mullin (1972) notes three different theories that account for crystal growth:

- surface energy effects
- adsorption layer
- diffusion

The surface energy theory assumes that crystals grow in the shape which has the lowest surface energy. The absorption layer theory suggests that:

> *"crystal growth is a discontinuous process, taking place by absorption where layer upon layer on the crystal is responsible for growth"*
> *(Bott, 1995).*

The diffusion is easiest to fit to fouling models. It states that crystal growth is proportional to the difference in concentration between the crystal surface and the bulk solution. In reality all three effects are important, although the growth of calcium phosphate crystals is surface reaction controlled in most situations (Marshall & Nancollas, 1969).

2.3.1 The Involvement of Proteins

Proteins are always present as a component in fouling deposits formed in UHT plants (Ito & Nakanishi, 1964; Nakanishi & Ito, 1966). It has been suggested that aggregation of proteins on the heat transfer surface is the controlling step in whey protein fouling (Lalande & Rene, 1988; Gotham *et al.*, 1989). Belmar-Beiny & Fryer (1993) examined the initial stages of WPC fouling to confirm that protein was the first species to form and examine the possibility that the induction period could be extended. They concluded that protein was the first species to adsorb in this situation, and calcium was not. However, this was based on XPS analysis showing low concentrations of calcium phosphate on the surface of the deposit, which increased towards the metal. This had been found earlier by Daufin *et al.* (1987). Although it is generally agreed that the layer of deposit closest to the metal is mineral in nature (Tissier & Lalande, 1986a; Foster *et al.*, 1989; Belmar *et al.*, 1994), this does not necessarily prove that minerals adsorb first. It may be that protein fouls first due to its high surface activity (Sandu, 1989), and minerals absorb later. As the process continues, the minerals migrate along the temperature gradient to the metal wall and create a region of high mineral concentration there. This can occur because the high temperatures next to the wall provide the point where the reverse solubility salt is most supersaturated.

In the end it appears that knowing which species fouls first is not likely to be important, although this is discussed later (section 6.7). Knowing this would only aid in lengthening the induction period, which is very small for dairy products. It is unlikely that it would be possible to extend this time enough to make it economically important. Since calcium phosphate is the major fouling component, understanding of the mechanisms that control this process is far more useful.

Protein fouling is well described by Fryer & Belmar-Beiny (1991). Deposit formation occurs as the protein denatures, and a complex series of reactions take place. The protein partially unfolds and exposes reactive sulphydryl groups. These either physically bond with the surface or to each other (aggregation). It has been speculated that this protein could catalyse later crystal growth (Lyster, 1965), but there is little proof of this.

2.4 Calcium Phosphate Chemistry

The structure and chemistry of calcium phosphate compounds has been studied since the 19th century, when the composition of many biological tissues were first discovered. Calcium phosphate is found in many different forms, those commonly found in milk systems are summarised in table 2.4.

Table 2.4 *Common forms of calcium phosphate*

Abbreviation	Technical Name	Formula
HAP	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$
DCPD	Dicalcium phosphate dihydrate	$CaHPO_4.2H_2O$
DCPA	Dicalcium phosphate anhydrous	$CaHPO_4$
OCP	Octacalcium phosphate	$Ca_8H_2(PO_4)_6.5H_2O$
TCP	Tricalcium phosphate	$Ca_3(PO_4)_2$
ACP	Amorphous calcium phosphate	N/A

It has been discovered that both teeth and bones were mainly composed of hydroxyapatite (HAP) (Zipkin, 1973; Posner, 1969; Hodgkinson & Nordin, 1968). Calcium phosphate is also present in saliva, urine and plasma, in concentrations well above its supersaturation point, yet no precipitation occurs (Nancollas & Tomson, 1976) (table 2.5).

Table 2.5 *A comparison of calcium concentrations in urine and whey permeate (after Nancollas & Tomson, 1976)*

Species	Urine	Whey Permeate
$[Ca^{2+}]$	0.88-7.8 mM (Elliot, 1964)	20 mM (Kellam, 1997)
Max. Sol. $[Ca^{2+}]$	0.3 - 6.0 mM	0.1 - 6.0 mM
$[PO_4^{3-}]$	20-50 mM (White *et al.*, 1973)	7.5 mM
pH	8.0 - 4.8 (White *et al.*, 1973)	5.0-6.5

In cow's milk 99% of the calcium is associated with the skim milk fraction (Fransson & Lonnerdal, 1983). Two thirds of this calcium is in the colloidal form associated with casein, mostly within a calcium phosphate salt. The other third is soluble (Holt, 1985; Peifang, 1994). A majority of the calcium in milk ends up in the whey permeate stream.

A lot of research has been performed which has attempted to understand the precipitation process of calcium phosphate. Although hydroxyapatite is the most thermodynamically stable form of calcium phosphate, it is not the form in which the first precipitation occurs. Various species have been found to be the first to precipitate. Dicalcium phosphate dihydrate (DCPD) (Francis, 1961), octacalcium phosphate (OCP) (Brown, 1966) and tricalcium phosphate (TCP) (Eanes *et al.*, 1967) have all been found as initial precipitators, depending on the pH and degree of supersaturation. The transformation of these phases to HAP is not understood, and thermodynamic investigations usually fail as kinetics are more important in this situation. This causes confusion when studying dairy fouling, as the phase that first deposits transforms before it can be analysed. The relative stability of the phases at various pH conditions are shown in figure 2.6 and table 2.6.

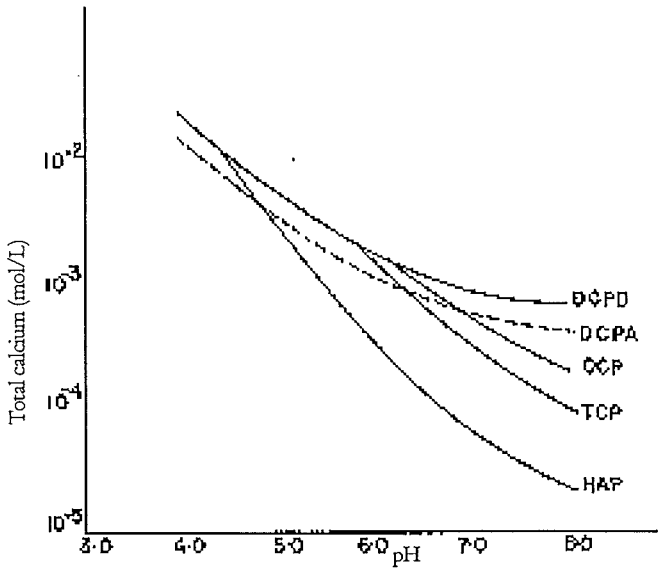

Figure 2.6 *Calcium phosphate solubility (Nancollas et al., 1979)*

The concentration of calcium in whey permeate is generally about 0.5 mol/L, well in excess of the solubility of any form of calcium phosphate. No precipitation occurs however, as much of the calcium is associated with the non-protein nitrogen species present and therefore has a lower activity than pure ionic calcium. This is discussed in section 6.7.

Table 2.6 *Solubility products of calcium phosphate compounds. (Nancollas et al., 1979)*

Compound	Solubility Product	Solubility Product (mol L^{-1})	Source
HAP	$[Ca^{2+}]^5 [PO_4^{3-}]^3 [OH^-] (\gamma_2)^5 (\gamma_3)^3 (\gamma_1)$	4.7×10^{-59}	McDowell *et al.* (1977)
TCP	$[Ca^{2+}]^3 [PO_4^{3-}]^2 (\gamma_2)^4 (\gamma_3)^2$	1.20×10^{-29}	Gregory *et al.* (1974)
OCP	$[Ca^{2+}]^4 [PO_4^{3-}]^3 [H^+] (\gamma_2)^4 (\gamma_3)^3 (\gamma_1)$	1.25×10^{-47}	Moreno *et al.* (1960)
DCPA	$[Ca^{2+}] [HPO_4^{2-}] (\gamma_2)^2$	1.26×10^{-7}	McDowell (1968)
DCPD	$[Ca^{2+}] [HPO_4^{2-}] (\gamma_2)^2$	2.49×10^{-7}	Patel *et al.* (1974)

Most of the research in this area has been undertaken from a medical perspective, in the hunt to understand gall-stone, teeth and bone formation. Some of this research has suggested (Nancollas & Tomson, 1976) that substances which are present in the body influence the nature of the phases initially formed. For example, phosphonate derivatives have been proven to be effective inhibitors of calcium phosphate crystal growth (Meyer & Nancollas, 1973) at very low concentrations. Pyrophosphate ions have been proposed as natural inhibitors in the body (Fleisch, 1964). It was found that concentrations as low as 10^{-6} mol L^{-1} can inhibit calcium oxalate precipitation (section 2.4.2). Conversely, fluorine as been found to act as a crystalline accelerator, even at low concentrations (Nancollas & Tomson, 1976) e.g., 0.15 ppm.

2.4.1 Calcium Phosphate Precipitation

Füredi-Milhoffer *et al.* (1976), discussed the two mechanisms that have been forwarded for HAP formation, at low levels of supersaturation.

1. Percussor seeds form first. Calcium deficient apatites form on these and are simultaneous hydrolysed to hydroxyapatites (Brown, 1965). This would explain why samples of calcium phosphates that are analysed are often found to have calcium/phosphorous ratios in the range on 1.33 to 1.67. This is less than the 1.67 expected for pure HAP (Termine & Eanes, 1972; Brown, 1965; Füredi-Milhofer *et al.*, 1973; Füredi-Milhofer *et al.*, 1971; Füredi-Milhofer *et al.*, 1975).
2. Noncrystalline calcium phosphate (amorphous calcium phosphate, ACP) is formed as an intermediate in the formation of apatitic calcium phosphate (Termine & Eanes, 1972; Eames & Posner, 1965). This postulate has not been checked.

Both of these mechanisms may be correct, as Füredi-Milhoffer *et al.* (1976) found that the type of phase that forms depends on the supersaturation present at precipitation. At low levels of supersaturation, direct crystallisation to the most stable phase will occur. This relates to the region of heterogenous nucleation and proceeds via the first mechanism above.

At high supersaturation, as found in whey permeate products, crystallisation proceeds via precursor phases as in mechanism two. These phases may be non-crystalline or a form of calcium phosphate that is less stable than HAP.

It was suggested by Sandu & Lund (1985) that the two hydrated salts DCPD and OCP are the first to precipitate as long as the level of supersaturation with respect to HAP is high. These deposits then gradually convert to the more stable calcium phosphate forms.

Füredi-Milhoffer *et al.* (1976) modelled DCPD growth in several pH environments. They found that precipitation was surface reaction controlled which agreed with previous research (Marshall and Nancollas, 1969). They suggested that the reaction was third order, although this conflicted with Marshall & Nancollas (1969) who found it was second order. The rate controlling step was postulated to be the adsorption and incorporation of DCPD molecules. It was also found that when the calcium phosphate solution was only minimally supersaturated, heterogenous nucleation occurred. When the solution was highly supersaturated, homogeneous nucleation occurred in the bulk of the fluid (section 2.4). The results found by Füredi-Milhoffer *et al.* (1976) pointed to a two or more stage precipitation process. The first step is the formation of ACP, which was then converted to a crystalline calcium phosphate like OCP or DCPA. This was by supported Sandu & Lund (1985) who claimed that ACP formed when the solution was so highly saturated that crystals did not have time to form, or when inhibitors were present to prohibit the formation of crystals.

Barton *et al.* (1985) attempted to examine the importance of all five solid forms of calcium phosphate, with little success. It was postulated that DCPD, DCPA and OCP acted as precursors for the later forming hydroxyapatite (HAP) (Barone & Noncollas, 1977; Nancollas, 1979; Marshall & Nancollas, 1969).

The huge range of theories and postulations point towards the crystallisation of calcium phosphate being a complex process influenced by pH, temperature and degree of supersaturation. It appears that when precipitation occurs in a moderately supersaturated solution like whey permeate a

crystalline form develops, as the concentration is not beyond the limit needed for ACP. This initial form is TCP when it forms in the pH range 5-6, which is typical for whey permeates, as this is the most soluble form in this situation (figure 2.6). This form rearranges itself over time to HAP, the most stable form, if water is available.

2.4.2 Phosphate Chemistry

A phosphate group consists of one phosphorous and four oxygen atoms, as shown in figure 2.7 below. The valency of phosphorous is 5, and oxygen 2, which means that the charge of the "extra bond" is spread around the four oxygens, so each atom has one and a quarter bonds.

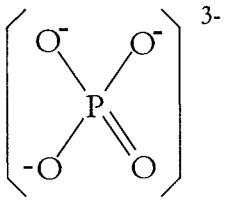

Figure 2.7 *Phosphate molecule*

All of the phosphate salts are built around this PO_4 tetrahedron. The oxygen atoms in this arrangement can be substituted for other elements (Averbuch-Pouchot & Durif, 1997). An example of a compound with this anion is $Ca_5(PO_4)_3OH$, otherwise known as hydroxyapatite (HAP). This is the most stable form of calcium phosphate, and is found in ultra-heat treated milk and whey permeate fouling.

Phosphates can be broadly classified into four groupings:

- monophosphates
- cyclophosphates
- condensed phosphates
- adducts

The first three type are discussed below.

Monophosphates

This name is given to all compounds whose anion is composed of $[PO_4]^{3-}$ (figure 2.8). The previous name of this grouping was orthophopshate, and it is still commonly used today.

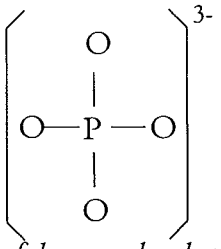

Figure 2.8 *The structure of the monophosphate/orthophosphate anion*

Cyclophosphates

These are cyclic condensation phosphates, and have the following anionic formula:

$$[P_nO_{3n}]^{n-}$$

The previous name for these compounds was metaphosphate, and this term is still commonly used. An example of a cyclophosphate is shown is figure 2.9 below.

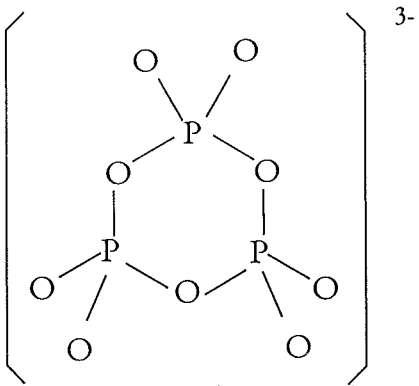

Figure 2.9 *The structure of the cyclotriphosphate anion*

Condensed Phosphates

This term is applies to anions which have an oxygen to phosphorous ratio less than 1:4. That is, at least one oxygen atom is bonded to two phosphorous atoms. The most important group of this type is the polyphosphate (figure 2.10). These are linear condensed phosphates containing at least two phosphorous atoms. The general formula for this group is:

$$[P_nO_{3n+1}]^{(n+2)-}$$

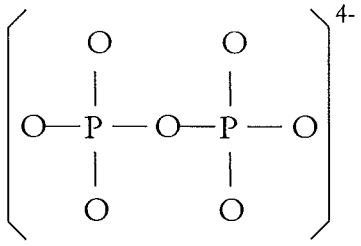

Figure 2.10 *The structure of the diphosphate/pyrophosphate anion*

If the number of phosphorous atoms present is five or less, then the polyphosphate is sometimes know as an oligophosphate. This is well summarised in Averbuch-Pouchot & Durif (1997) and presented below (table 2.7).

Table 2.7 *Naming scheme for linear phosphates (after Averbuch-Pouchot & Durif, 1997)*

# Phosphorous Atoms	Anion	Technical Name	Common or Brand Name
2	$[P_2O_7]^{4-}$	Diphosphate	Pyrophosphate
3	$[P_3O_{10}]^{5-}$	Triphosphate	Triphosphate
4	$[P_4O_{13}]^{6-}$	Tetraphosphate	Tetraphosphate
7	$[P_7O_{22}]^{9-}$	Heptaphosphate	BUDIT 7H
16	$[P_{16}O_{49}]^{18-}$	-	BUDIT 16H

All three fouling inhibitors investigated were condensed phosphates. Sodium pyrophosphate (diphosphate) is a condensed phosphate with two phosphorous atoms. BUDIT 7H and BUDIT 16H are the brand names for a mixture of condensed phosphates of average chain lengths 7 and 16 respectively.

Burdett (1974) proposed that tetrasodium pyrophosphate could be used to inhibit fouling in ultra-heat treated milk plants (section 2.4.3) The structure diagram of the diphosphate anion is shown in figure 2.10 above. The $Na_4P_2O_7$ salt has been chemically characterised since 1816 (Averbuch-Pouchot & Durif, 1996), and is known to have six crystalline forms. The anhydrous form is extremely hydroscopic, and therefore the atomic arrangement of its atoms has not been studied. The decahydrated form, $Na_4P_2O_7.10H_2O$ is very stable and has been well studied. It is assumed that this is the form that has been obtained from J. C. Sherratt & Co, Ltd (Christchurch, New Zealand), although the sample has not been labelled as a hydrated form.

2.4.3 Use of Additives to Alleviate Fouling

Three phosphates were considered as potential additives to alleviate fouling: tetrasodium pyrophosphate, BUDIT 7H and BUDIT 16H. It is not known exactly how these compounds inhibit fouling, although three hypothesises exist.

Nancollas *et al.* (1979) suggested that inhibitor molecules take the place of a normal phosphate anion $(PO_4)^{2-}$, and effectively interrupt the ordered crystal pattern. The phosphate must then either stack on top of the inhibiting ion, or develop a new nucleation site (figure 2.11). Both of these alternatives have higher energy requirements than ordered precipitation. Leung & Nancollas (1978) proved that only 4% of the surface of barium sulphate crystals need to be covered by phosphates, for complete inhibition of crystal growth to occur. It is believed that this is due to precipitation occurring at only a tiny number of active sites.

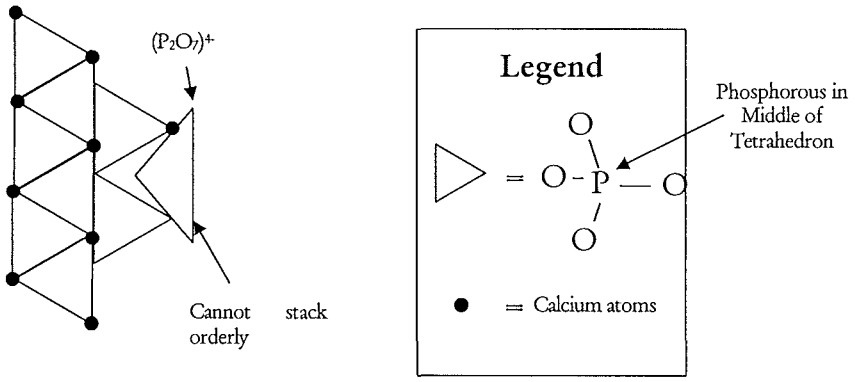

Figure 2.11 *Representation of $(P_2O_7)^{4-}$ inhibition of $Ca_3(PO_4)_2$ precipitation*

The second theory proposed that additives bind the free calcium ions. It was claimed that calcium ions denature whey proteins during heating (Schnee, 1997), and binding the calcium stopped this occurring. This mechanism has not been proposed elsewhere.

A third theory is more likely. It proposes that additives stabilise the calcium content of the whey permeate, by forming phosphate complexes with higher solubilities at the processing temperatures. Chemische Fabrik (CFB Budenheim, Germany) market a full range of phosphates through J.C. Sherratt & Co Ltd (Christchurch, New Zealand). It has been suggested that companies in America and Europe already use these additives (Hoogenboezem, 1997).

Burdett (1974) studied the effects of adding five different polyphosphate compounds to milk and skim milk before UHT processing. Sodium pyrophosphate was included in the study. It was found

that sodium pyrophosphate ($Na_4P_2O_7.10H_2O$) appeared to inhibit fouling more than the other test substances. Sodium pyrophosphate treated whole milk took 60 minutes to reach a pressure differential of 100 kPa in a plate heat exchanger, whereas untreated milk could only be processed for 18 minutes until reaching this pressure. Unfortunately, the validity of these results is questionable, since Burdett (1974) reported that the processing time for unadjusted whole milk to reach 100 kPa varied between 16 to 48 minutes, depending on what day the tests were conducted. This was blamed on daily variation, but this is far more than other researchers have found between seasons (Burton, 1967). The results are reproduced in table 2.8 below.

Table 2.8 *The inhibition effect of phosphates on dairy fouling (Burdett, 1974)*

		Time (min) to reach pressure differential of 100 kPa				
		Whole			Skim Milk	
Phosphate Added	Conc. Additive % (w/w)	Day 1	Day 2	Day 3	Day 4	Day 5
None	-	48	18	16	60	64
$Na_4P_2O_7.10H_2O$	0.0025			20		
	0.0075			24		
	0.01		35	32		
	0.05		47			
	0.10		60		102	
$(NaPO_3)_6$	0.10	54				
$Na_5P_3O_{10}$	0.10	58				76
Na_2HPO_4	0.10	58				92
NaH_2PO_4	0.10	58				

In the same research, tests were performed on the resistance changes in a heated platinum wire suspended in milk. The findings from this experiment were presented in terms of K, which is the relative susceptibility to fouling buildup. These results also showed $Na_4P_2O_7.10H_2O$ is the best inhibitor, reducing the K value by 60% for whole milk, and by 25% for skim milk. The other test substances showed very similar results, reducing fouling by 40% for whole milk, and 20% for skim. Unfortunately these results were generated using a platinum wire, which has very different flow and surface characteristics to the wall of a stainless steel evaporator tube. Also, all tests were conducted using a 0.01% concentration of phosphate which is a tenth of the concentration that is suggested for industry situations (Hoogenboezem, 1997).

Burdett explained the fouling inhibiting properties of the phosphate additives as being due to protein stabilisation. As the milk is heated, the reverse solubility salt calcium phosphate is precipitated, which will reduce the concentration of phosphate in solution. This then 'leaches' phosphate from the casein micelle (Davies & White, 1959). The partially destabilised casein micelles would then be liable to coagulate and form deposit. It is suggested that the addition of soluble phosphates increases stabilisation by shifting the micelle phosphate equilibrium in the favourable direction. This would explain the reduction in proteinacous fouling when processing milk, but not that observed in the low protein fouling of whey permeate.

Burdett mentioned that previous researchers (Campbell & Nancollas, 1969; Miura & Naono, 1965) have found that pyrophosphate ions reduce the precipitation of sparingly soluble salts. The studies suggested that since the calcium phosphate in urine and plasma is supersaturated, they inhibit precipitation in blood or the urinary tract.

Marshall & Nancollas (1969) found that the rate of growth of crystals of DCPD was reduced by addition of pyrophosphate at concentrations as low as 10^{-6} M. They suggested that the strong inhibiting effect was caused by the formation of a monomolecular blocking layer of foreign ions at the crystal surface. However both this research and that of Campbell & Nancollas (1969) and Miura & Naono (1965) did not investigate polyphosphates.

Heng & Glatz (1991) looked at the addition of EDTA for calcium chelation in wheys. It was found to be useful in alleviating ultrafiltration fouling, but only when added in an equal molar ratio to the calcium present.

3 Introduction to Whey Permeate Processing

Dairy products are a vital part of the New Zealand economy, making up over 20% of all exports. Whey permeate can be considered as the final stream from a long series of processes, which remove the components from milk step by step. Whey permeate contains high levels of lactose, as well as minerals and non-protein nitrogen (table 3.1). Lactose is removed and sold as a crystalline powder, mainly used in the pharmaceutical industry as an encapsulate in pill production. It also has uses as a food ingredient, in whole and skim milk standardisation and as a caking inhibitor (Moss, 1933).

Table 3.1 *The composition of cheddar cheese sweet whey permeate (Kellam, 1997; Zadow, 1992)*

Component	Composition
Total Solids	5.8 %
Lactose	4.8 %
Non-Protein Nitrogen	0.5 %
Minerals	0.5 %
Fat	Trace

Non-protein nitrogen (NPN) refers to protein fragments, urea (H_2NCONH_2), peptides, vitamins and amino acids. Although these components are referred to as non-protein nitrogen sources, this is confusing terminology. Protein fragments can actually be classed as proteins, but are often dismissed as NPN due to their small size when compared to casein or whey proteins. The confusion is created because there is no formal size cut-off between a protein and a peptide, although several hundred amino acid units is commonly used. Therefore, some of these so called 'NPN' components could be considered proteins and their behaviour reflects this.

3.1 Review of Dairy Processes

Whey permeate is a byproduct of several dairy processes, as shown in figure 3.1.

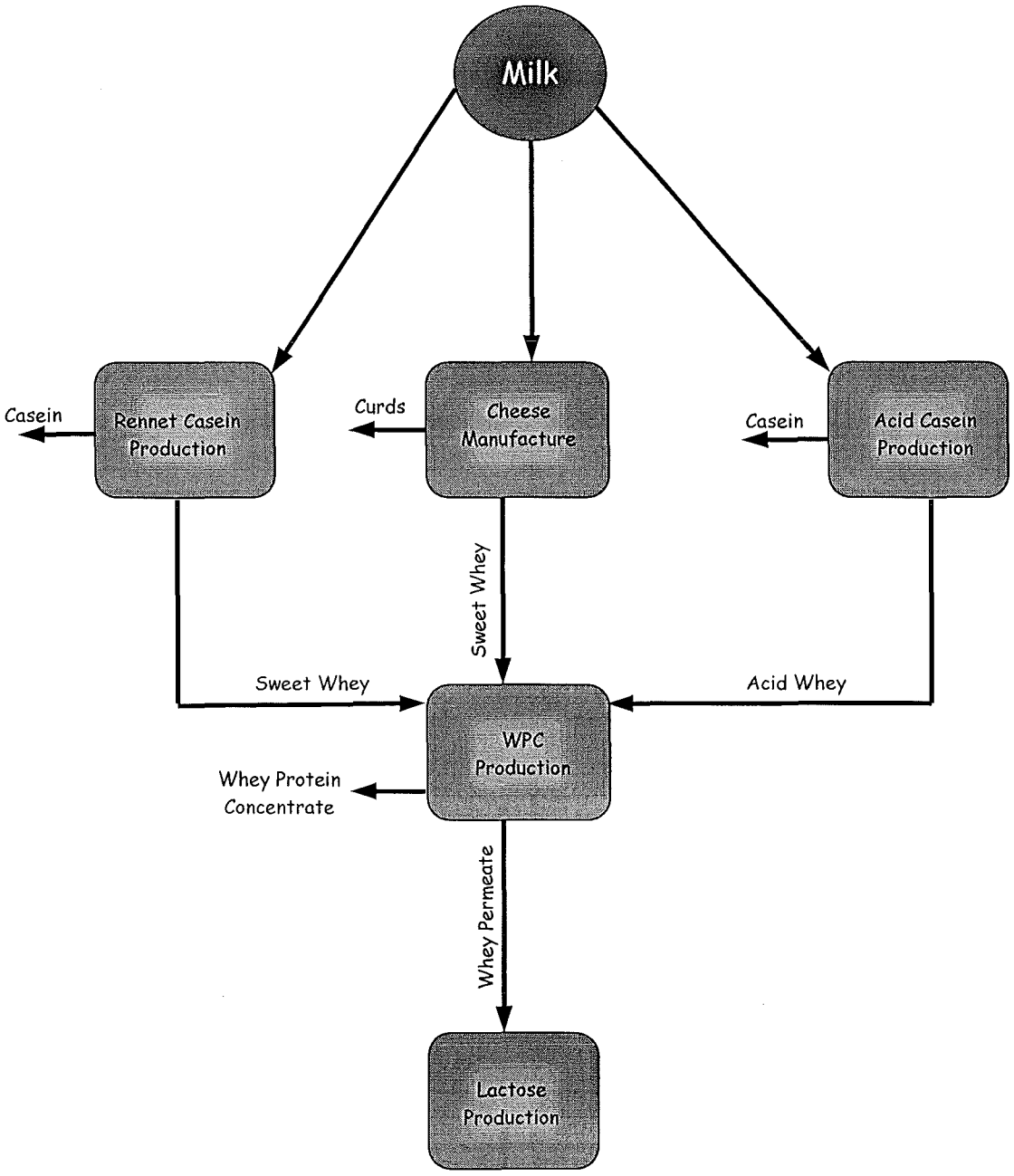

Figure 3.1 *Common dairy processes which lead to lactose production*

Of the total volume of milk made into cheese and casein, 80-90% will leave the process as whey, and this whey will contain approximately 40-50% of the original total solids (Nielsen, 1996). Since such a large proportion of the raw milk coming into a dairy process leaves as whey, the processing of this by-product is of great interest to the dairy industry. In the past whey has sometimes been seen as a troublesome waste product, and has been sprayed on fields or used as animal feed. With the development of new separation technologies this has changed. The production of spray dried whey protein concentrate (WPC) and lactose by crystallisation has now taken place for many years.

There are two main types of whey: sweet whey (also know as cheese whey or rennet whey), and acid whey. Sweet whey is formed from traditional cheese making and also in the production of rennet casein. It has a pH of above 6.0. Acid whey has a pH of around 4.5, and results from production of casein using acid, and production of cottage or fresh cultured cheese. Table 3.2 below shows a summary of the composition expected in milk, sweet whey and acid whey.

Table 3.2 *Average composition of various wheys and milk (Nielsen, 1996)*

	Milk (% T.S.)	Sweet Whey (% T.S.)	Acid Whey (% T.S.)
Total Solids	13.0	6.4	6.2
Protein	3.6	0.8	0.75
Fat	3.9	0.5	0.04
Lactose	4.6	4.6	4.2
Ash	0.8	0.5	0.8
Lactic acid	-	0.05	0.8

Whey contains proteins of high nutritional value, and these can be concentrated and made into whey protein concentrate. This process is shown in figure 3.2.

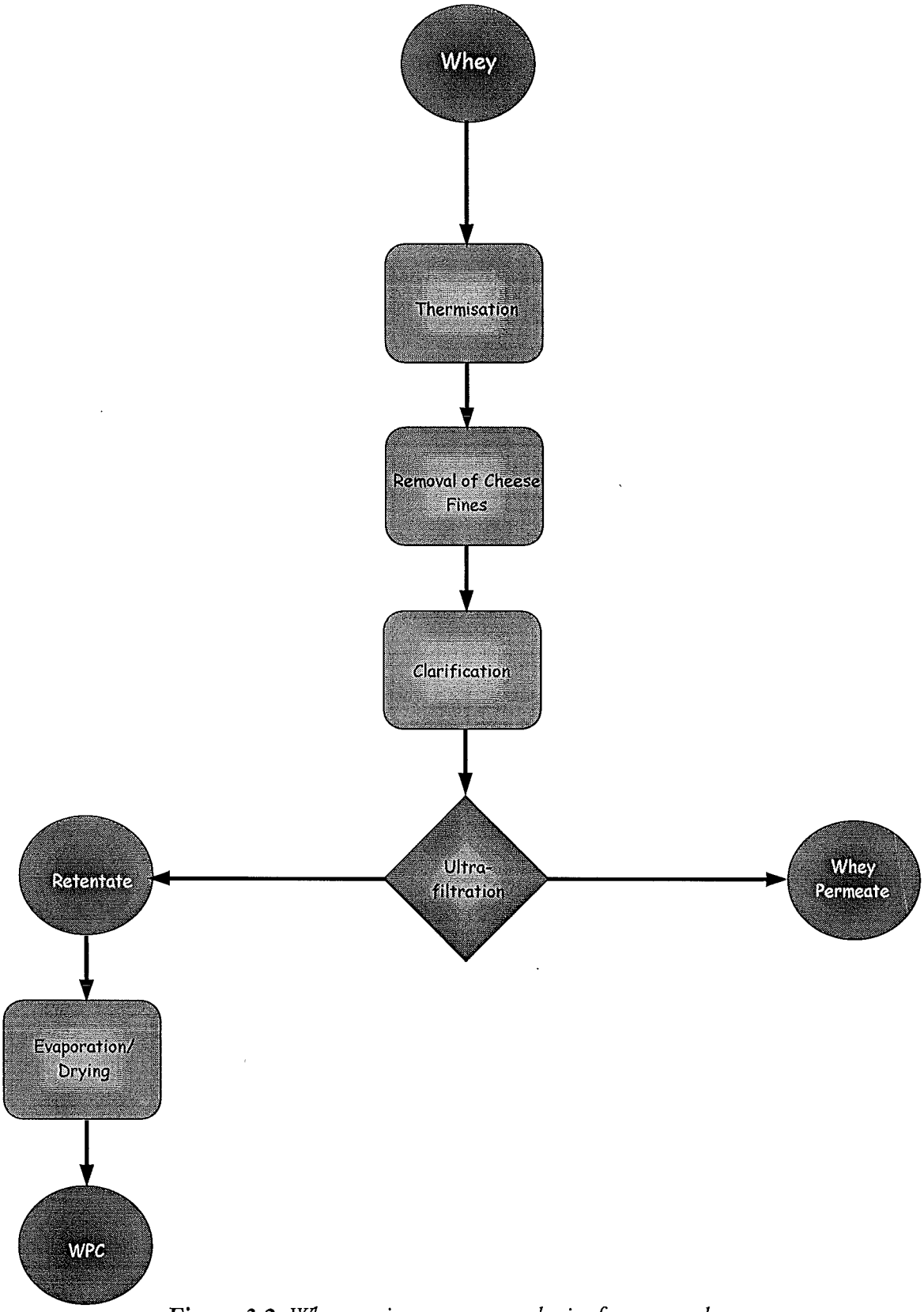

Figure 3.2 *Whey protein concentrate production from sweet whey*

Whey permeate is made in the WPC process when whey is ultrafiltered. The retentate has a high concentration of whey proteins, the permeate is mainly lactose and minerals. Typically 80-85% of the solids in this permeate are lactose and 8-10% are minerals (Nielsen, 1996; Kellam, 1997). Vitamins, small proteins that may have got through the ultrafiltration, peptides and non-protein nitrogen containing components (such as amino acids) are also present.

This whey permeate has a number of uses. It can be used to standardise the protein contents in milk, especially in the making of milk powders. It can be dried to form lactose powder which is used in the pharmaceutical industry.

3.2 Review of the Lactose Production Process

The process by which lactose powder can be made from whey permeate is shown in figure 3.3.

The whey permeate is first concentrated up to 12% total solids (T.S.) by reverse osmosis. It is then concentrated to 45-50% T.S. via evaporation. This is the processing step where a majority of the calcium phosphate in the whey permeate precipitates, and the biggest fouling problem occurs. At Lactose New Zealand, two five-effect falling film evaporators are used in parallel for this primary evaporation. The product is then passed through to further evaporation stages, which increases the concentration to 62-68% T.S. At this stage the lactose concentration is high enough that when seed crystals are introduced, it instantly precipitates. This occurs in the crystallisers.

The lactose sludge is then passed through a series of decanters and washing cycles to purify it. The final product is dried, milled and packed.

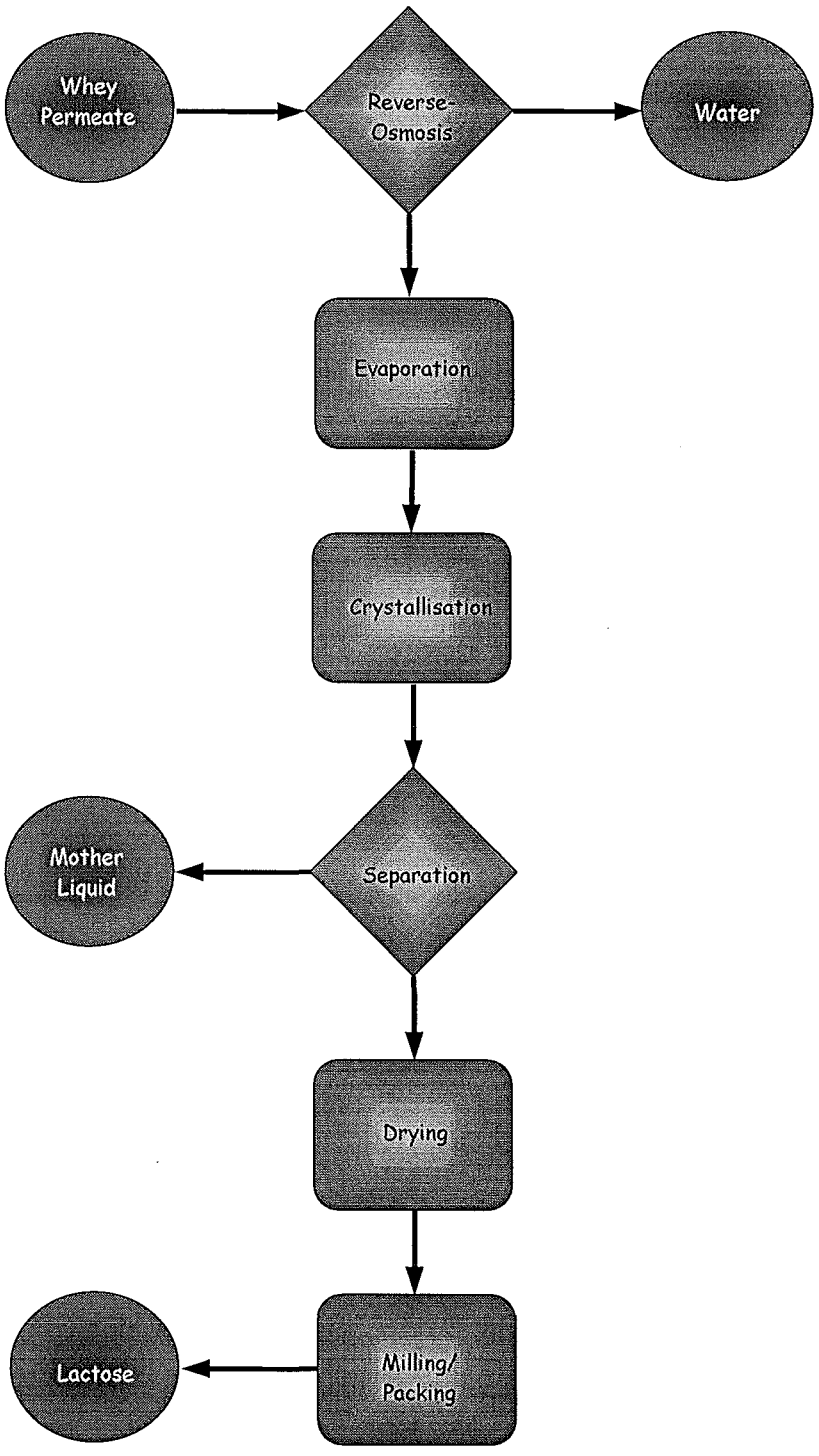

Figure 3.3 *Lactose powder production from whey permeate*

3.3 Evaporator Technology

Evaporation is the process of removing water by boiling. This chapter only deals with the aspects of evaporator design that affect fouling. Billet (1989) and Nisenfield (1985) both give excellent wider introductions.

In lactose production, evaporation is used to concentrate whey permeate to the point where crystallisation can occur. Although many forms of evaporators have been developed, falling-film evaporators are almost the only type found in the dairy industry (figure 3.4).

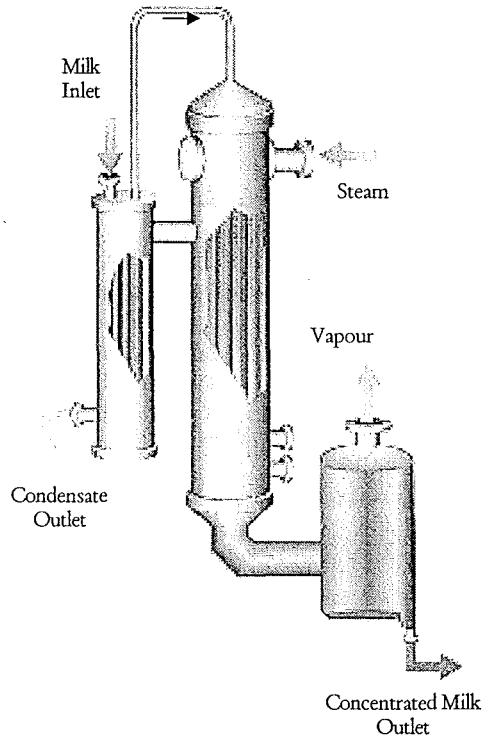

Figure 3.4 *A falling-film evaporator (Bylund, 1995)*

Falling-film evaporators provide very short residence times and operate well under vacuum. This means that they are perfectly suited for processing heat sensitive products. Since dairy fluids are very sensitive to heat effects, falling-film evaporators are used extensively in dairy plants world wide.

Falling-film evaporators operate by spreading the incoming product evenly across the tubes of the tube bundle or calandria. This is achieved by using a distribution plate system which can range

from a complex device to ensure each evaporator tube receives equal flow, to a sheet of metal with holes in it (figure 3.5)

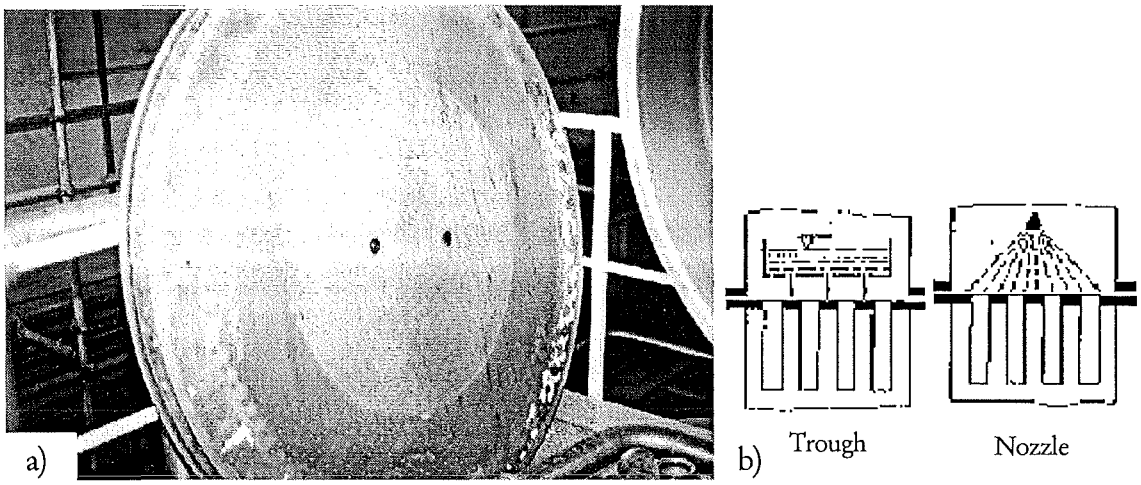

Figure 3.5 *Distribution devices. a) Simple distribution device (Lactose New Zealand) b) Trough and nozzle device (Billet, 1989)*

The key to success in falling-film evaporators is good distribution of the feed over the entire heat transfer surface (Bylund, 1995). Without this individual tubes can experience 'dry-on', which causes sever fouling. Dry-on occurs when all of the water flowing down a tube is evaporated, leaving behind all the solids it contained on the tube walls. Once this occurs, it tends to lead to more fouling, as the deposit will divert flow away from that area by acting as a dam. Eventually the entire tube can become blocked.

Another important requirement in distribution plate design is vapour downcoming space (Bouman *et al.*, 1988) (figure 3.6).

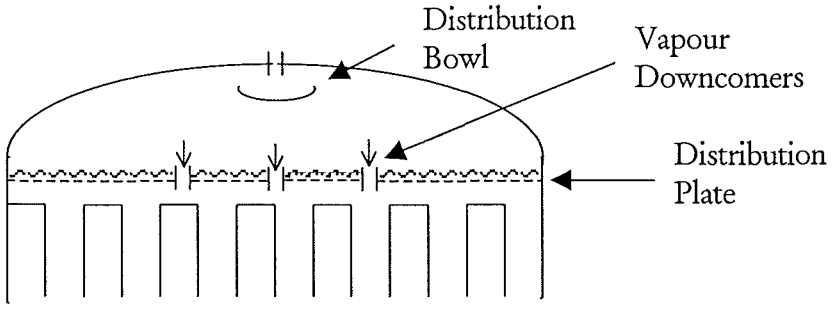

Figure 3.6 *Distribution device with vapour downcomers*

The feed into evaporators is superheated, and as soon as it enters the chamber at the top of the evaporator body some of it instantaneously boils into steam (flashes). This is important, as the vapour flow rate it creates forces the remaining liquid against the tube walls, and tends to spread it

evenly. However, if no allowance is made in the distribution plate for this vapour to escape, it builds up in the top of the body and creates pressure on the surface of the liquid (figure 3.7a).

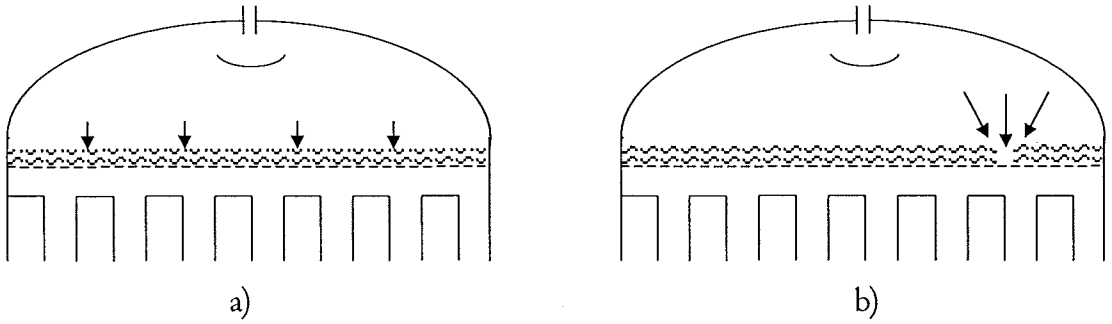

Figure 3.7 *Buildup of pressure on liquid head above evaporator distribution plate*

The pressure builds and forces the liquid through the distribution plate, rather than letting it distribute evenly. Eventually the pressure becomes high enough that the vapour can force its way through, at the expense of the surrounding liquid (figure 3.7b). Once this occurs the vapour will tend to escape through the same spot, starving one part of the evaporator of fluid. This increases the chances of dry-on mainly in this area, but the whole evaporator is effected as other areas will not have as much vapour to spread the flow evenly over the tube walls.

As the vapour escapes the pressure drops and eventually the liquid closes over the gap and totally covers the distribution plate again (figure 3.7a). The pressure builds until this process repeats. The spot where the flash vapour breaks through is random since the hydrodynamic conditions are so complex. Therefore a different region of tubes is placed at risk each time this occurs, and many different areas can experience dry-on due to this effect. This leads to extensive fouling.

The evaporators used in the primary stage of whey permeate concentration generally have about five effects (figure 3.8).

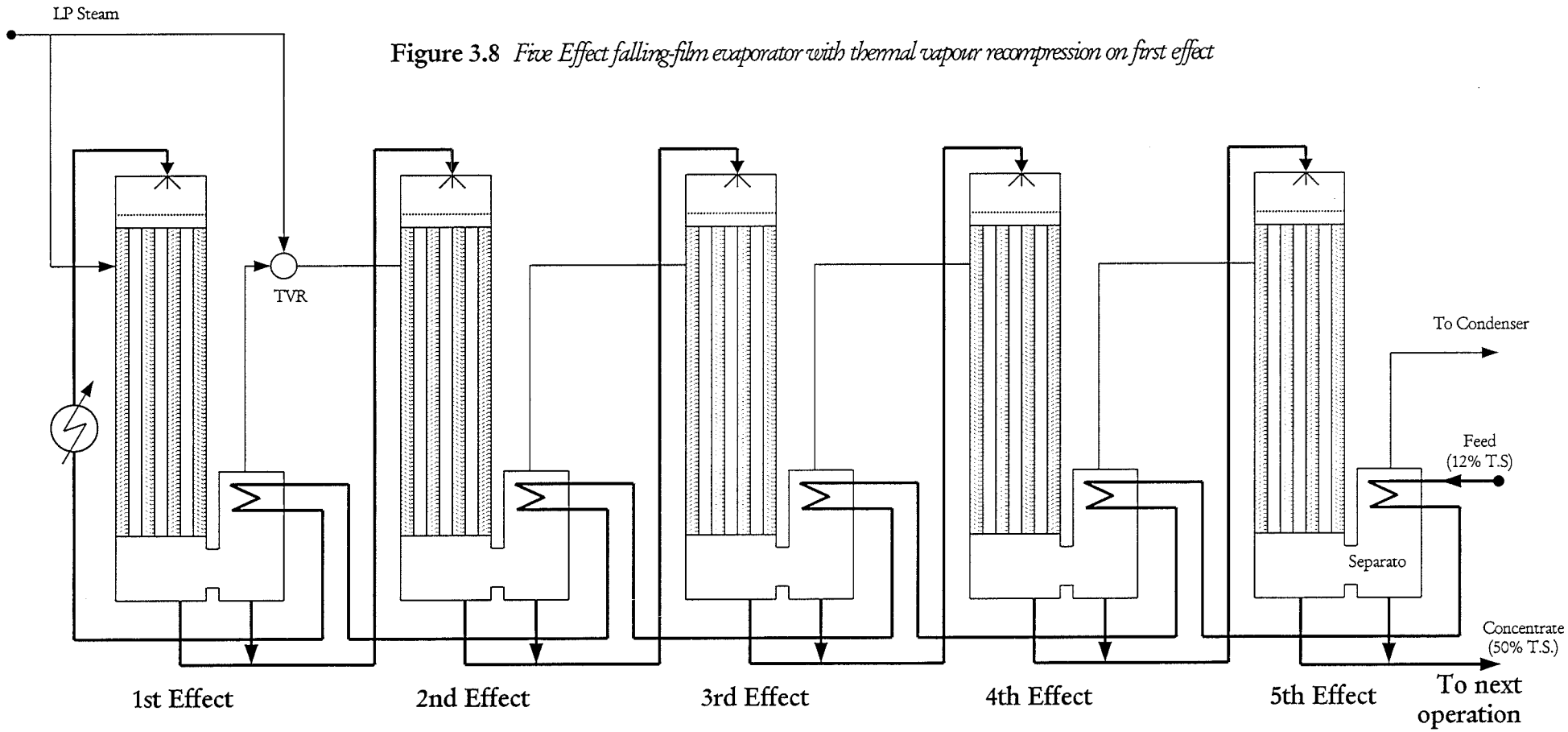

Figure 3.8 *Five Effect falling-film evaporator with thermal vapour recompression on first effect*

In this configuration, the product to be concentrated is first passed through the separator of each effect. This uses energy from the outgoing vapour, and increases the temperature to ~70°C. The feed is then passed through a preheater which increases its temperature to ~80°C. The whey permeate is then pumped into the top of the first effect. Some of the feed flashes as it enters because this effect operates at 43 kPa (boiling point 78°C). This tends to spread the feed. The product is further spread by a distribution bowl directly below the entry point (figure 3.6).

This is simply a hemisphere of metal with holes in it, which reduces the momentum of the feed and scatters it onto the distribution plate. The distribution plate spreads the product evenly across the tubes, which the liquid flows down. On the other side of these tubes is steam at a temperature of 90°C. The steam condenses, and transfers energy to the lower temperature product, which boils. The vapours from the boiling whey permeate collect in the centre of the evaporator tubes, and move quickly down to the bottom of the effect to escape. As they do this they spread the remaining liquid against the tubes walls, in the same way the flash effect does.

The vapour and concentrated liquid reach the bottom of the evaporator, and pass through a rectangular duct to the separator along side (figure 3.9).

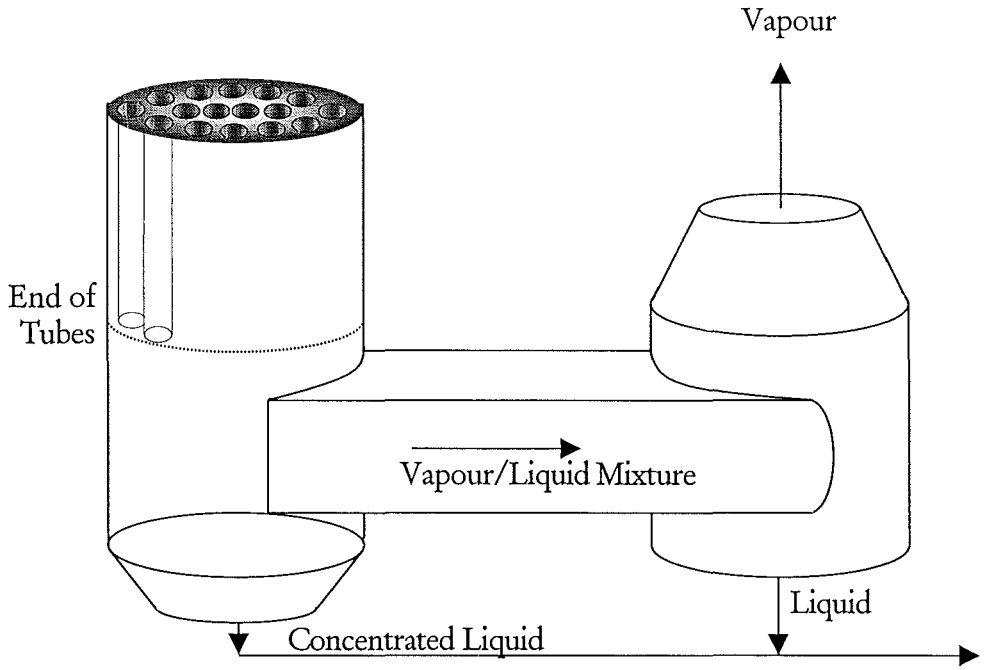

Figure 3.9 *Bottom of evaporator with separator*

The separator is a high speed cyclone, which separates any entrained liquid from the vapour by using centrifugal force. The liquid is collected from the bottom and pumped to the top of the next effect. The vapour is removed from the top. This vapour contains large amounts of energy, but its 'quality' is low since it is at a low pressure and temperature. To rectify this, the steam is 'recompressed', i.e., has its pressure increased. This is done by mixing it with higher quality steam, in a thermal vapour recompressor (TVR) (figure 3.10).

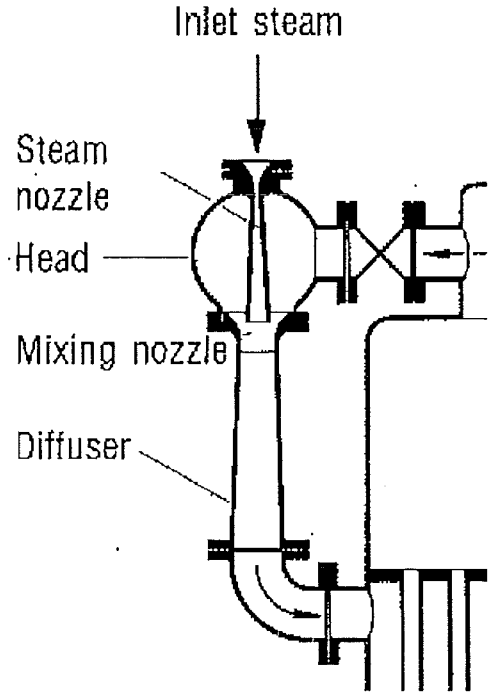

Figure 3.10 *TVR (Thermal vapour recompressor) (Billet, 1995)*

A TVR allows the vapour from the first effect to boil the liquid in the second effect, because the 2nd effect operates at a lower temperature (e.g., ~70°C). In theory the heat of vaporisation remains almost constant with pressure, therefore there is enough energy in the 1st effect vapours to boil an equal amount of liquid in the second effect. But this will not occur unless there is a temperature differential for the energy to travel across. To be of practical use, this temperature difference has to be at least 10-15°C, otherwise the heat transfer area must be large. This means the TVR must be used to recompress the vapour from ~78°C (45 kPa) to ~85°C (58 kPa). This provides a ΔT of ~15°C, which boils some of the liquid in the second effect. The vapour condenses, and is collected. This is termed 'foul condensate' as it contains some volatile dairy residues. These emit a strong odour, and require waste water treatment for removal.

At the bottom of the second effect the concentrated liquid and vapour are separated again. The liquid is sent to the top of the third effect, the vapour may be recompressed and sent to the steam side of the third effect. This cycle continues, until the last (fifth) effect. Here the liquid leaves at around 50% T.S. and the vapours are sent to another part of the plant for use.

Another method which is used to save energy is mechanical vapour recompression (MVR). This is when the vapours from an effect are increased in pressure by using large mechanical compressors. For a review on this process see Nisenfeld (1982).

3.4 Demineralisation

One method of reducing the fouling problem caused by minerals is to remove them prior to the evaporation stage. This results in reduced downtime and chemical costs.

Although whey permeate may contain a lower level of minerals than whey, pre-treatment is often needed to avoid excessive scaling of the evaporator. This particularly applies to acid whey permeate, as its ash content is higher and it contains a greater amount of calcium salts. (Nielsen, 1997).

3.4.1 Heat and pH Treatment

Precipitating the calcium salts prior to evaporation can control the fouling problem. This involves using a holding section, and directly heating the whey permeate to at least 60°C. As the walls of the holding tube are not heated, nucleation tends to occur in the bulk of the fluid.

Calcium content can be greatly lowered by addition of alkali and holding at a raised temperature. At pH 8, over 80% of the calcium in lactic casein whey permeate can be removed at 70°C with 8 minutes holding (Hobman, 1984). (figure 3.11).

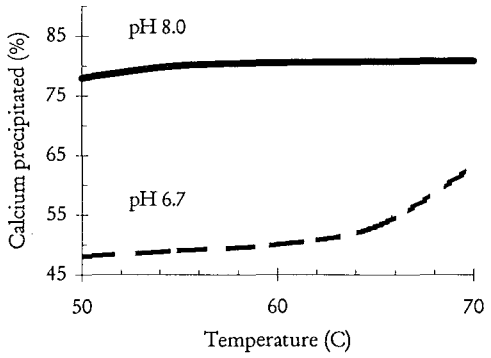

Figure 3.11 *Precipitation of calcium phosphate at a holding time of 8 minutes (Hobman, 1984)*

This method is already partially being used at Lactose New Zealand. A heating system and holding tube is used to dissolve lactose crystals that form during transportation. This process would have an added effect of precipitating a small amount of calcium salts, prior to evaporation. It has been reported that whey permeate treated with this processing step appears to foul less than untreated permeate, although this has not been tested (Styles, 1997).

Adding sodium hydroxide until a pH of 8.0 is reached means that approximately 80% of the calcium can be precipitated at temperatures of 50°C or more.

However, more mild pH and heat treatments can also be effective. Hobman (1984) reports that pilot scale trials showed that a 50% reduction in calcium was enough to prevent evaporator fouling during subsequent concentration.

The advantage with this demineralisation technique is that far less capital investment is needed than either ion exchange or electrodialysis systems (Hoppe, 1992). The moderate levels of demineralisation that it produces can be effective at reducing evaporator and heat exchanger fouling (Daufin *et al.*, 1987). This technique is most effectively applied to permeate, as whey proteins appear to inhibit the precipitation (Brule *et al.*, 1978; Schmidt & Both, 1987).

There are several problems that have caused this method to not be used in the dairy industry. Holding at elevated temperatures can gives rise to 'burnt' flavours in the final product, which is undesirable when producing milk powder. Although this is unlikely to be a factor in lactose production, Malliard browning of the sugar in whey permeate may occur. This would cause slight off-colouring in the final product. However Lactose New Zealand has developed a process

modification which over comes this problem. In the past, control of residence time distribution and difficulties during start-up were also concerns, but these have largely been overcome by modern control methods (Hasting & Goederen, 1988).

3.4.2 Nanofiltration

Nanofiltration (also know as ultra-osmosis, 'loose' reverse osmosis or NF), is a process which has characteristics similar to those of both reverse osmosis and ultrafiltration. This process used membranes which have excellent salt passage properties when applied to whey or whey permeate, but retain almost all of the lactose (figure 3.12).

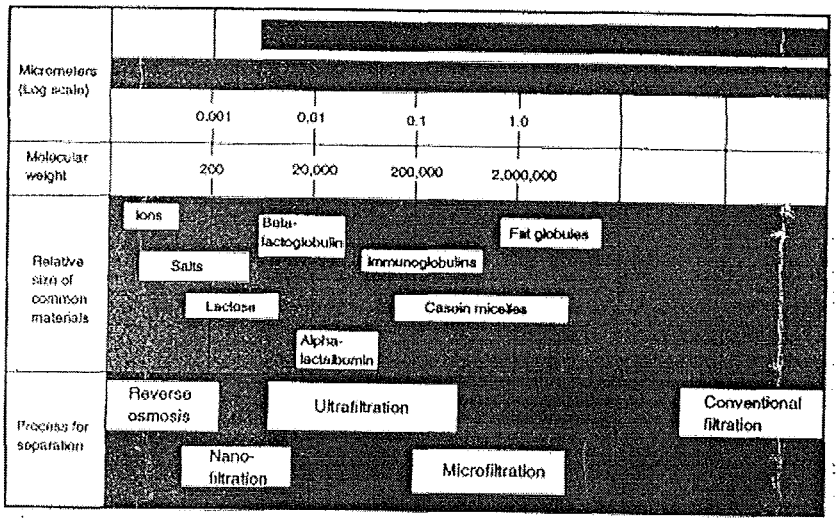

Figure 3.12 *Relative cutoff points for membrane operations (Bennett, 1996)*

It is reported that at a concentration factor of 4, demineralisation of 30-35% can be reached. This can be increased to 40-42% using diafiltration (Nielsen, 1996). This method also uses about 10 to 20 times less water than ion exchange or electrodialysis. Average rejection characteristics are presented in table 3.3, where magnesium sulphate is the best guide of how much calcium phosphate would be rejected.

Table 3.3 *Average rejection characteristics for a NF membrane (Neilsen, 1996)*

	Molecular Mass	Rejection (%)
Salt (NaCl)	58	45
Calcium chloride	111	70
Magnesium sulphate	120	98
Glucose	180	90
Sucrose	342	98
Raffinose	504	99

This method has been applied to saltly whey (Gregory, 1986), and its use advocated for whey or ultrafiltration permeates (Hutson, 1986). Nanofiltration would also allow partial removal of low molecular weight organics. These compounds can cause browning of lactose crystals in the final product.

This method is capital intensive. The prices for nanofiltration membranes are several times that of ultrafiltration membranes. The permeate from this process would also contain high levels of minerals, and would be difficult to treat.

Running costs of NF plants are high due the high processing pressures (25-30 bar) needed, and hence high pumping energies are needed. Nanofiltration also allows univalent ions to pass easier than divalent and larger ions. It can be seen in table 3.3 that Na^+ and Cl^- can pass easily, while Ca^{2+} is retained (Scott, 1995). This is unfortunate as the calcium is the species that needs to be removed to reduce fouling. 70-85% of the minerals removed are the monovalents that do not contribute towards fouling.

Bennet (1996) describes an industrial plant which is used to demineralise and concentrate lactic whey permeate before evaporation. It is noted that the partial demineralisation reduces scaling, but the permeate stream contains some lactose which has to be removed before discharge. This plant uses 1,340 m^2 of membrane area to process 72,000 L/hr. By direct scaling it can be seen that a plant which needs to process 40,000 L/hr would require 770 m^2 of membrane. The capital requirements of such a large area of membrane would be in the order of $500,000 including installation costs. This price is prohibitive considering the high running costs (e.g., pumping) that

are also present, and the low selling price of lactose. Nanofiltration is not a suitable method of demineralisation to reduce fouling.

3.4.3 Ion Exchange

The process of ion exchange is the most well known of the demineralisation technologies. It has the ability to remove almost all of the minerals present in whey and permeate (Hoppe, 1992; Food Manufacture, 1980).

The process operates by passing whey through a bed of cationic resin which is initially saturated with H^+ ions. The dissociated cations in the whey, such as sodium, potassium and calcium are exchanged for hydrogen ions. The whey is then directed through an anionic resin bed, which removes the dissociated anions such as chlorides and sulphates. These are replaced with hydroxyl groups.

Once the resin beds are saturated with ions, they are regenerated by passing a high concentration of their counter ion through them. Acid is used for a cationic exchange resin, alkali for an anion resin.

Ion exchange is the most expensive method of mineral removal presented here, but also allows the highest demineralisation (table 3.4). Unfortunately, ion-exchange would require very short cycle times due to the high salt content of whey permeate (Scott, 1995). Therefore, large amounts of chemical regenerates and water would be required.

3.4.4 Electrodialysis

Electrodialysis is a process in which the ionic components of a solution are separated under the influence of an electrical driving force (Mason & Juda, 1959). The transport of ions is made selective by barriers which are only permeable to ions of certain size and charge. It is only commercially viable to remove up to 50% of the minerals in whey by electrodialysis (Nielsen, 1996; Hoppe & Higgins, 1992). More monovalent ions than polyvalent ions are generally removed. This will change the mineral profile of the product.

Membrane fouling is a large problem with this process. Precipitation of calcium salts often occurs at the cationic membrane, especially when operating close to the limiting current (Korngold *et al.*, 1970; Young, 1974). These precipitates cause scaling on the surface of the membranes which may be removed by normal acid cleaning conditions.

Undesirable loss of components can also occur. Lactose and non-protein nitrogen (NPN) losses can occur through direct transport of these components through the membrane. It is reported that at 90% demineralisation, NPN losses are about 25% (Delaney, 1976) and lactose 6% (Delbecke, 1975; Delaney, 1976; Evans, 1985). Electrodialysis is usually performed after pre-concentration of whey (Scott, 1995) to increase the ion concentration and therefore reduce processing costs. Previous workers have found that capital costs make this process unprofitable (Short & Doughty, 1977; Short, 1978) and it has therefore not been investigated further.

Table 3.4 *Demineralisation Processes Summary. (Hoppe & Higgins, 1992)*

	pH and Heat Treatment	Nanofiltration	Ion Exchange	Electrodialysis
Minerals Extracted	Calcium salts	Favours monovalent ion removal	Similar levels of all dissociated ions removed	Similar levels of all dissociated ions removed
Max. Demin.	40-50%	40%	<95%	50%
Losses	NPN Lactose denaturation	NPN Small amounts of lactose	2.5-3% solids loss 30% NPN loss	Leakage losses Lactose transfer through membranes
Water Requirements	None	Soft water	Soft water	Soft water
Chemicals	Alkali	CIP	Regenerants for resins	CIP
Total Effluent	High pH mineral stream	Permeate and chemicals	7.8 kg salt/m^3 whey	Up to 5000 mg/litre BOD
Capital Cost	Low	Moderate	High	High
Operating Cost	Low	Moderate	High	High

4 Experimental Methods

The aim of this project was to investigate whey permeate fouling in evaporators. To do this the composition and magnitude of fouling on stainless steel was studied under conditions simulating those found in industry. After studying the attempts of previous researchers (Burton, 1965; Tissier & Lalande, 1986a; Kastanas *et al.*, 1995; Truong, 1997), it was decided to build a device that drew inspiration from the research of Davies *et al.* (1997) as shown in figure 4.1.

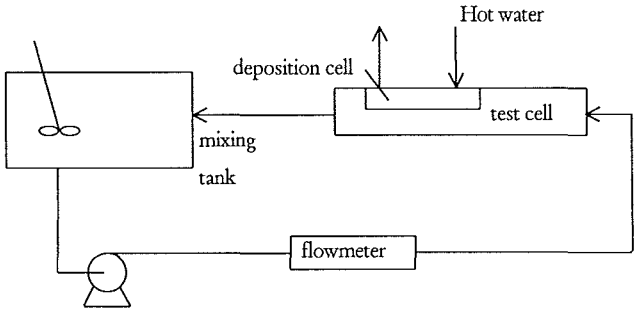

Figure 4.1 Experimental apparatus of Davies *et al.* (1997)

Their device was used to investigate fouling of horizontal stainless steel in full channel flow conditions. The device for this project needed to simulate a vertical thin film flow, as found in evaporator tubes. This was achieved by taking the device shown in figure 4.1 and building it on the vertical, along with extensive modifications. This is shown in figure 4.2.

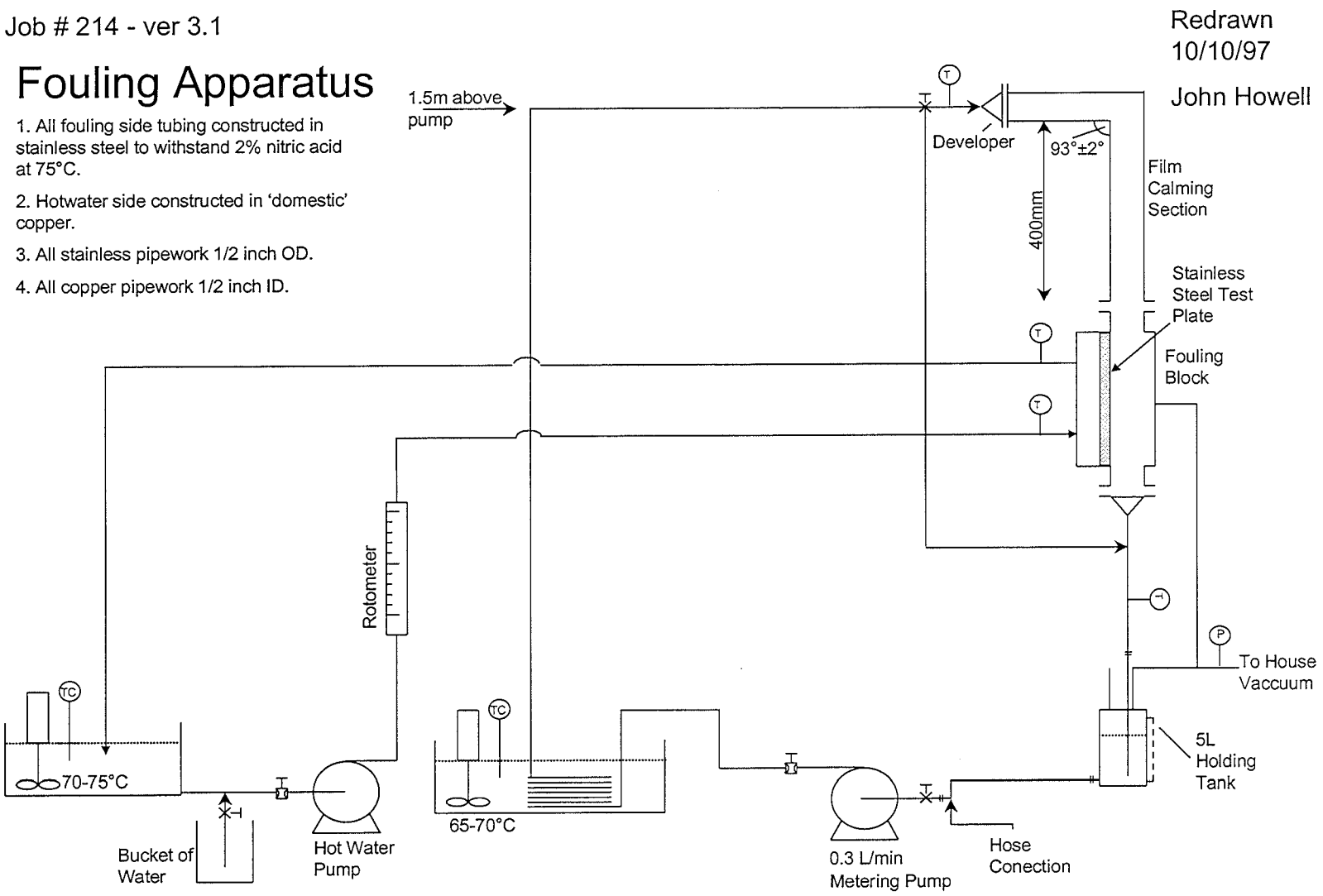

Figure 4.2 *Fouling Apparatus*

To begin operation, whey permeate was placed in the 5 L holding tank. The fluid was then drawn into a peristaltic ball-valve pump, and forced through 1.5 m of stainless steel coil in a water bath. This simulated the effects of a preheating stage on the feedstock. The water bath was kept at 60°C for a majority of the experiments. The whey permeate was then pumped up 1.5 m to the top of the apparatus, and the flow allowed to pass through a development section. This was designed to convert a round pipe (1/2 inch OD) into a square section (20 mm by 20 mm) over a distance of 60 mm. The flow then fell down a 400 mm long 'film calming section', which allowed a thin film to develop.

This film was then passed over the test plate, the back of which was heated with hot water, simulating the steam side of an evaporator tube. The water temperature was 75°C for a majority of the experiments. The temperature was assumed to be constant at all points on the back of the plate, as the 'steam side' flowrate was extremely high.

After passing over the test plate, the whey permeate emptied back into the holding tank. The inflow and outflow positions were keep separate so that the feedstock mixed well before re-entering the flow loop.

The stainless steel plates used were 159 mm by 69 mm ±0.5 mm with a thickness of 1.10 mm ± 0.05 mm. The heat transfer area was 130 mm by 40 mm, or 52 cm^2. Grade 316 stainless steel was used, which is the same material as the evaporator tubes at Lactose New Zealand. All test plates were sanded with 600P grit paper to give them a surface finish similar to an industrial evaporator. The plates were then washed, rinsed with distilled water and dried at 105°C overnight. After removal from the oven, samples were allowed to reach room temperature before weighing on a Sartorius balance (0.1 mg). Test plates were placed in the fouling unit and distilled water flushed over them for several minutes to make sure the entire surface was wetted before whey permeate was processed. After fouling, the test plate was carefully removed and placed in an oven at 105°C overnight before weighing. A set of standard operating procedures for this device can be found in appendix D.

To best examine what was happening in Lactose New Zealand's evaporators, the operating conditions of the first effect of the 'Scheffiers' evaporator were closely mimicked. This unit operation usually operates at a pressure of ~40 kPa, so that the boiling point of the processed solution is ~75-78°C. The feed is introduced into this system at a temperature slightly above the

boiling point, so that a proportion 'flashes' (instantaneously becomes steam) on entry. This flash was not modelled in this project, for reasons discussed in section 6.1. The flowrate in a typical evaporator at startup is generally about 40,000 L/hr. In the experimental rig this is equivalent to 0.340 L/min (or pump setting 3.8). Appendix A shows the calculations of this scaling. As flow rate has an effect on fouling (Gordon *et al.*, 1968), the flow rate was held as constant as possible.

In a typical evaporator, the longitudinal (from top to bottom) temperature rise is very small, perhaps 2-3°C over 10 m. This is controlled by pulling a vacuum on the unit, which forces liquid to evaporate after this small rise. As the fouling test block in this investigation was run at atmospheric conditions, the temperature rise over the 130 mm of heating surface was 2-3°C.

Calcium phosphate solutions were made as per the method of Daufin *et al.* (1987). Appendix E describes this process in more detail. All chemicals were analytical grade (99.5%) and obtained from BDH Laboratory Supplies (Poole, England).

4.1 Heat Treatment Methods

To mimic an industrial scale heat treatment process, a water bath was brought up to the appropriate temperature (either 60°C or 80°C). Two 500 mL stainless steel beakers with 1 mm wall thickness were then placed in the bath until they reached thermal equilibrium. Whey permeate was poured into each beaker and a stopwatch (0.01s resolution) started. Temperature readings were taken with a thermocouple connected to a Fluke meter (0.1°C resolution) every half minute during the processing. The solutions were vigorously agitated with a glass stirring rod to ensure that T_{wall} approached T_{bulk} as closely as possible. This provided a uniform temperature in the solutions.

Using this method it was possible to heat whey permeate solutions moderately quickly. The speed of heating was well below that obtainable in an industrial situation, as dairy pasteurisers can heat solutions to ~73°C within a few seconds. This research therefore, will produce results which underestimate the effect of preheating. To reduce this level of underestimation somewhat, the time data was adjusted so that only the period which the fluid spent above 50°C was considered to have contributed to the preheating. This temperature is shown to be the point at which large scale precipitation begins (section 3.5) and this method is further discussed in section 4.2.

4.2 X-ray Photoelectron Spectroscopy (XPS) Preparation

Samples were cut into 20 mm^2 squares and dried overnight. During this process, care was taken so that no fouling broke off and the sample surface was not touched in any way. Samples were analysed at the University of Auckland on a Kratos XSAM 800 apparatus, the simulatory anode being Magnesium. A 5 mm^2 area of each sample was analysed with an excitation current of 12 mA and voltage of 14 kV. A depth profile was gained by spluttering the sample with an ion beam. This allowed determination of composition through the thickness of the deposit. Skoog & Leary (1992) give a good summary of this analytical method.

4.3 Scanning Electron Microscope (SEM) Analysis

Samples were dried overnight and then carbon coated. Carbon rather than gold coating was used so that an elemental analysis could be conducted. A JEOL JSM-6100 scanning microscope (Mechanical Engineering, University of Canterbury) with an acceleration voltage of 20 kV was used for all samples, except those that had been heat treated and centrifuged (section 5.1.8). These samples were only covered by a thin layer of fouling, and started to heat and crack at this voltage. For these samples 2 kV was used. Elemental analysis was carried out at 20 kV.

4.4 Optical Microscope Examination

Samples were analysed and photographed on an Olympus BX60 optical microscope.

5 Results

5.1 Whey Permeate Fouling

The whey permeate used in the research came from two sources. The first whey permeate was Kiwi Dairies Ltd cheese whey permeate, which had been passed through a WPC process and then concentrated from 6% to 12% T.S. using reverse osmosis. The second source was from the New Zealand Dairy Group's (NZDG) Hautapu site. It was 12% T.S. cheddar cheese whey permeate, which had received the same concentration treatment as the Kiwi RO permeate. These two whey permeates will be referred to as "Kiwi permeate" and "Hautapu permeate". Unless otherwise noted, the experiments used a flowrate of 0.340 L/min, contact time of 1.5 hours, steam side temperature of 75°C and preheat temperature of 60°C.

5.1.1 Different Sources

The fouling of Hautapu permeate was first compared to Kiwi permeate. The results are shown in figure 5.1 below.

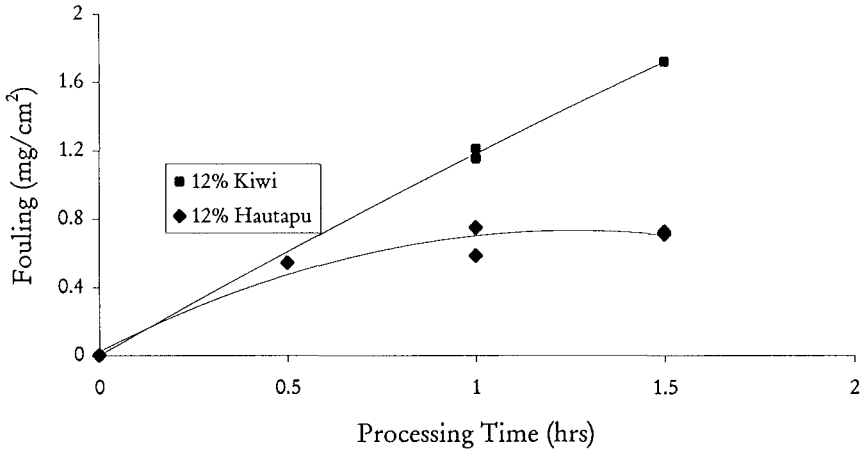

Figure 5.1 *Fouling of various whey permeates with respect to processing time*

It can be seen that Kiwi permeate fouls significantly more than whey permeate sourced from Hautapu. Both permeates were preserved with exactly the same method (addition of 0.1% thymol). NZDG whey permeate is never processed by Lactose New Zealand in the form it is analysed here, as it is concentrated to 50%T.S. at Hautapu to save on transport costs. It is interesting to note that the Hautapu site is reported to have had less problems with whey permeate fouling than LNZ, and the evidence above would support this. This is probably due to Kiwi Dairies using a 'cold' UF process and is discussed in section 6.7. It is also possible that storage time is an important factor. This is discussed in section 6.3.

5.1.2 Processing Time

Hautapu permeate was processed for varying times and the results graphed below (figure 5.2). These experiments were performed over two consecutive days to minimise the storage effects (figure 5.2).

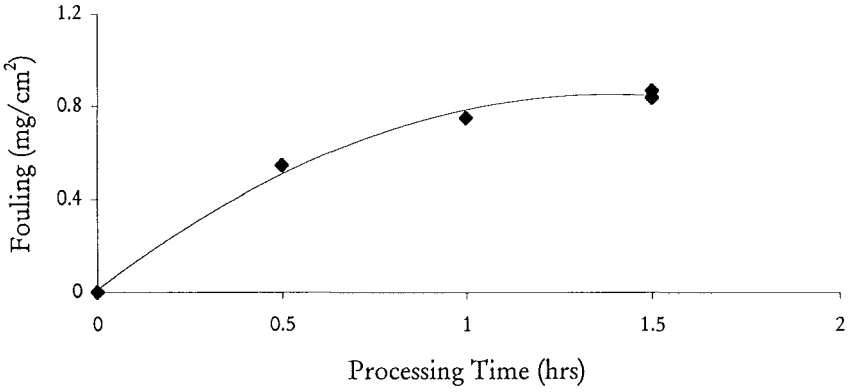

Figure 5.2 *Fouling at various processing times*

This data was generated using the standard operating conditions presented in section 5.1. The fouling shows an asymotopic relationship with respect to fouling time as described by Bott (1995). It is important to note that this experiment was run as a batch process, using 1 L of starting feedstock. A deposit of 0.8 mg/cm^2 equates to 42 mg of calcium which accounts for only 6% of the calcium in Kiwi permeate. This shows that not all of the calcium has precipitated after a run of 1.5 hrs, although the heat treatment may have changed its form (section 6.2).

5.1.3 Storage Time

Fouling changed with storage time before processing as shown in figure 5.3 below.

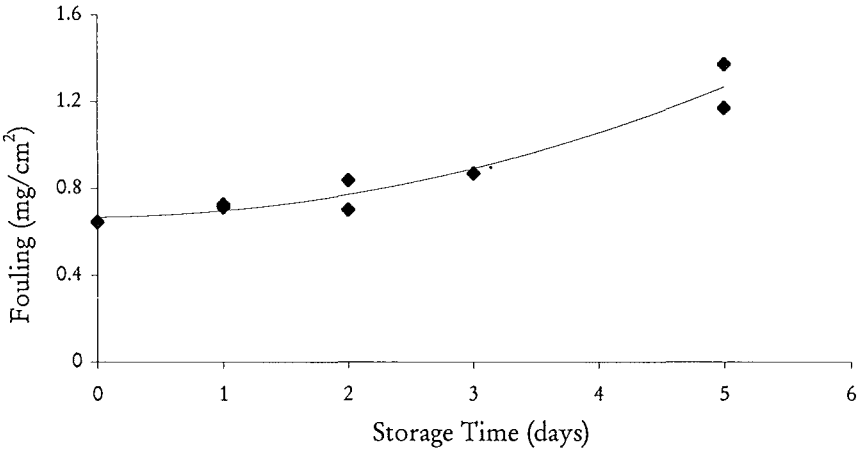

Figure 5.3 *Fouling of whey permeate with respect to storage time.*

This data was generated using Hautapu permeate and the standard conditions noted in section 5.1.2. Storage time slightly increases the amount of fouling in the short term. It is possible that the whey permeate that was obtained from Kiwi was already several days old, and therefore more likely to exhibit heavy fouling. The Hautapu permeate used was sent directly to the University of Canterbury after collection, and was only two days old when received. Figure 5.3 also shows the importance of processing whey permeate as soon as possible after it arrives on site. Minimising time before processing would be beneficial in reducing fouling.

This trend does not agree with what is observed by operators at Lactose New Zealand. It is widely believed that permeate stored for an extended length of time becomes "easier to deal with" (Woodshead, 1997). This discrepancy is due to the storage times shown above all being less than one week. When Hautapu whey permeate was held at room temperature for approximately one month, fouling was not observed. This would agree with what is seen when intermediate product (50% T.S.) is held in bunkers at LNZ during the summer months for off-peak processing. This whey permeate is regarded as giving longer run times, although no numbers can be provided to prove this. Section 6.3 deals with reasons the storage time displays this trend.

5.1.4 Plate Temperature

One of the first factors investigated was the effect of plate temperature on fouling. It was hypothesised that there is a minimum temperature below which no fouling would appear on a plate. Figure 5.4 shows the results of this investigation.

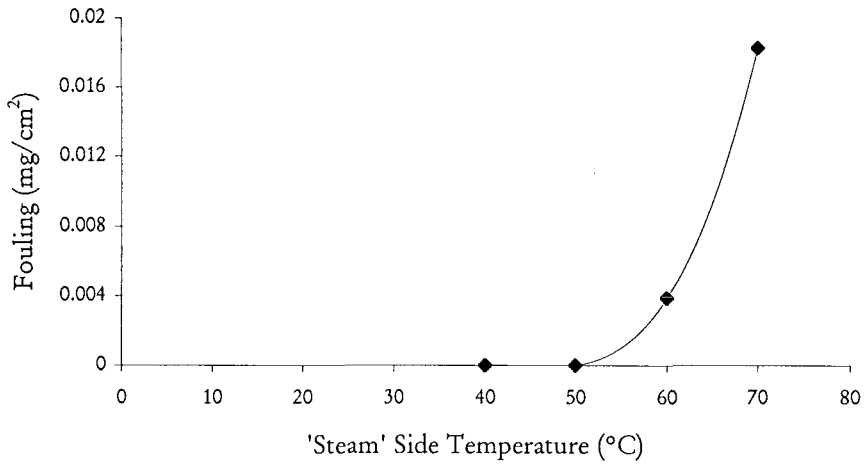

Figure 5.4 *Effect of plate temperature on whey permeate fouling*

The data clearly shows that fouling will not occur below a temperature of about 60°C. Below this calcium phosphate is not destabilised enough to crystallise on the plate surface.

The results in figure 5.4 were obtained using a preheat temperature of only 25°C. This is why the level of fouling is remarkably less than seen in the other experiments. This preheat temperature was chosen so that only wall temperature effects would be important.

5.1.5 Preheating Time and Temperature

This work provided a starting point for investigations in the effects of preheating. 60°C was chosen as a starting point, as this appeared to be the lowest temperature where preheating would be effective (figure 5.5).

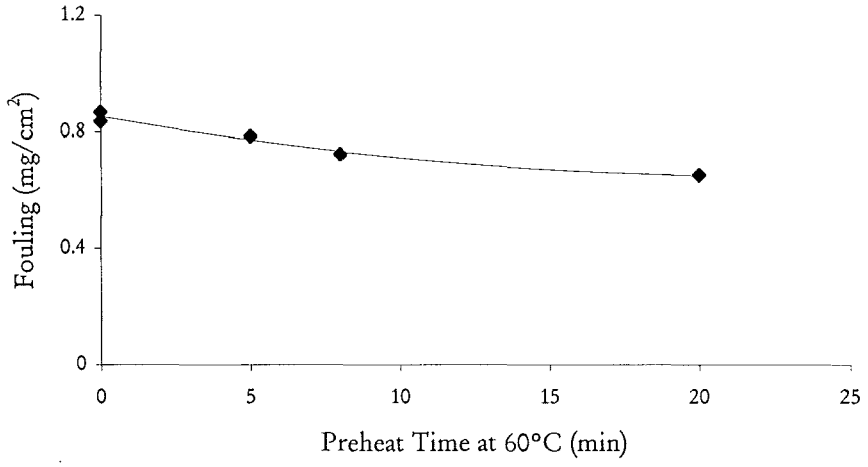

Figure 5.5 *Fouling of Hautapu whey permeate after preheating at 60°C.*

It can be seen that heat treatment at this temperature does not cause a large reduction in fouling. Even with preheating time of 20 minutes, which would be impossible in an industrial situation, fouling is only reduced by 24%. Preheating at 80°C was then investigated (figure 5.6). The temperature range of 70-80°C is where denaturation of dairy proteins begins to occur very quickly (Hillier & Lyster, 1979).

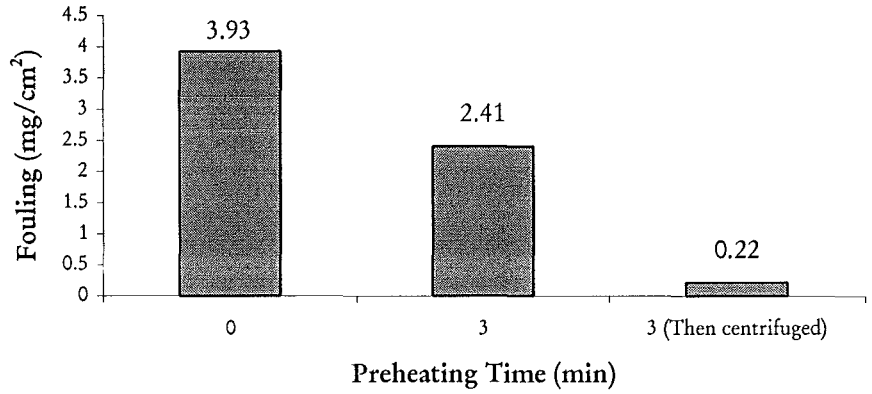

Figure 5.6 *Effects of centrifuging and preheating at 80°C*

This temperature reduced fouling by 39%, but it was noticed during preheating that large flocculants of calcium phosphate formed in solution. During processing, this appeared to bond to the surface of the stainless steel test plate. To alleviate this, one batch was centrifuged at 630 g for 3 minutes before processing. Fouling was then dramatically reduced by 94%, and the calcium phosphate precipitate recovered. This method is very effective at alleviating fouling, and would not cause problem down stream in the process with crystallisation as discussed in section 6.4 (Thomas, 1998). The Hatapu permeate that was used for these tests had been stored for several days which accounts for the high level of fouling observed (figure 5.6). The pretreatment experiments were performed within one day of each other to minimise storage effects.

5.1.6 Visual Inspection

The fouled plates were examined using an optical light microscope. This revealed the texture of the deposit surface and also indicated if crystal formation had occurred. Unfouled stainless steel is shown in figure 5.7.

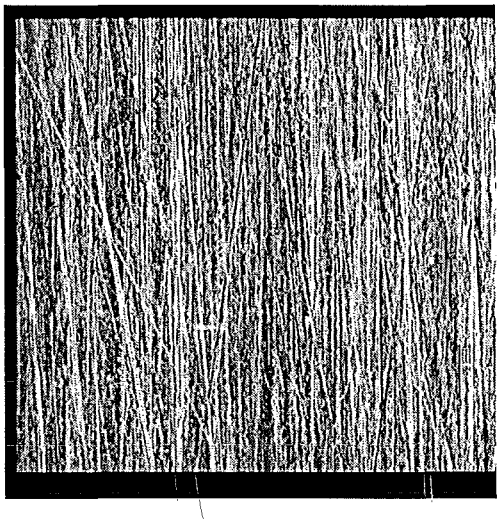

Figure 5.7 *Unfouled stainless steel plate (10x)*

The etching from buffering with 600P grit paper is clear. This is close to the texture of an industrial evaporator after several years of use.

Figure 5.8 shows the dense fouling observed when whey permeate is processed without pretreatment. The cracking is due to drying at 105°C overnight. Before drying the fouling has a continuous, unbroken texture. This is seen in figure 5.9.

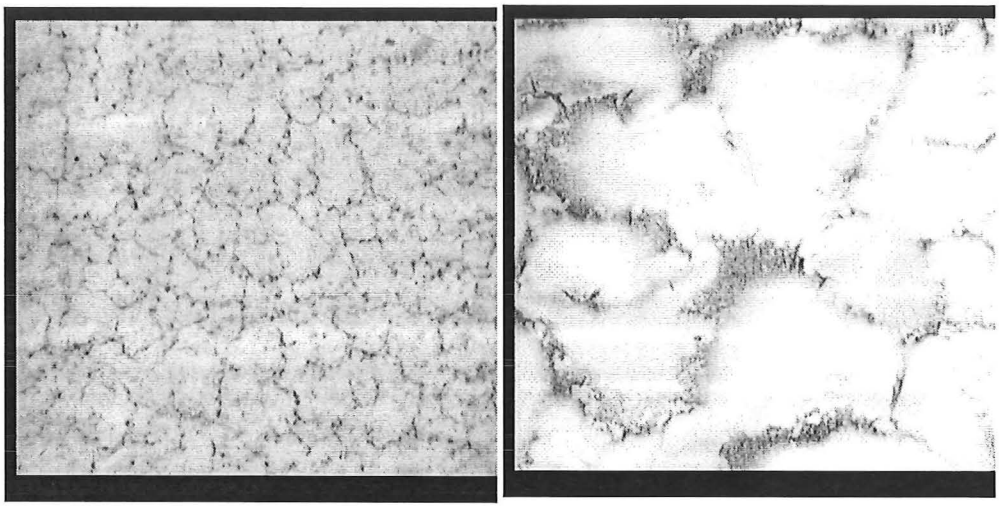

Figure 5.8 Fouling from whey permeate (no preheat) (a) 5x (b) 10x

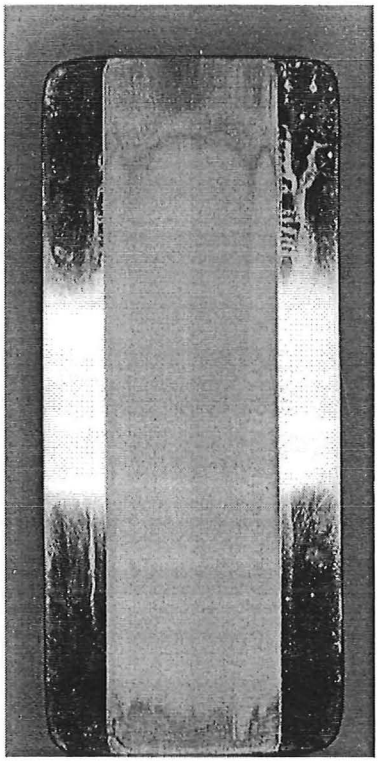

Figure 5.9 *Whey permeate fouling on test plate (no preheat)*

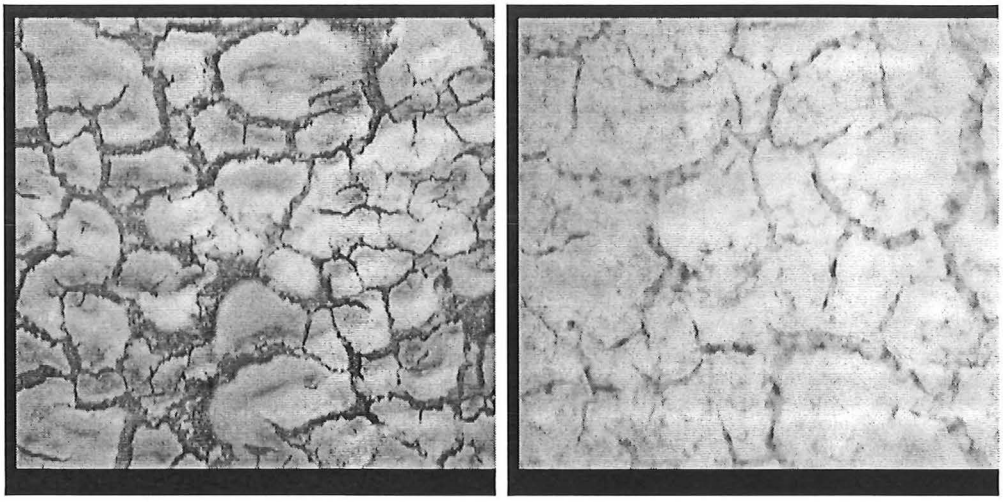

Figure 5.10 *Fouling from heat-treated whey permeate after drying (a) 5x (b) 10x*

Fouling of heat-treated whey permeate is different to untreated feedstock. The fouling layer consisted of a much chunkier texture, which was clearer before drying (figures 5.10 and 5.11). Preheat conditions were 80°C for 2 minutes.

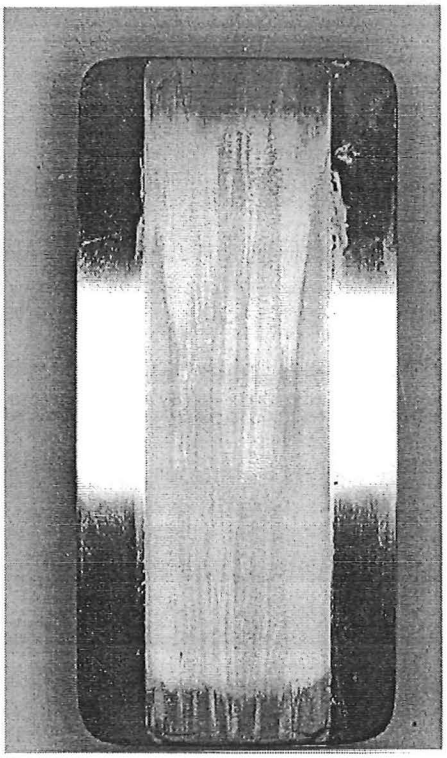

Figure 5.11 *Fouling of heat-treated whey permeate*

It appears that calcium phosphate crystals which precipitated during the heat treatment were able to latch onto the stainless steel plate later. For this reason preheating by itself is not an effective alleviation method (section 6.4).

When whey permeate was heat treated and then centrifuged, a calcium phosphate sludge was recovered. Whey permeate processed after this treatment exhibited very little fouling, although the stainless was still covered by a very fine white film. This is shown in figures 5.12 and 5.13. The pretreatment conditions were 80°C at two minutes, then 630 g for two minutes.

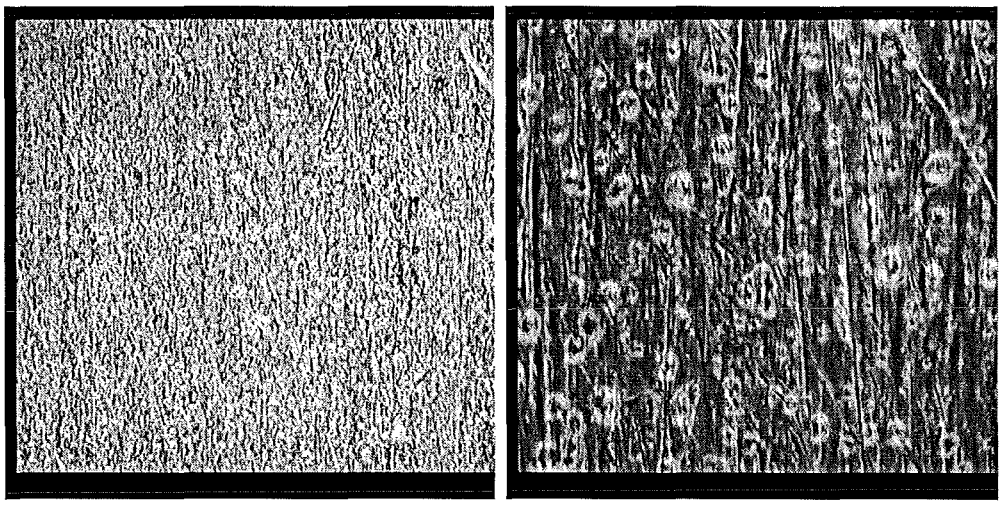

Figure 5.12 *Fouling from heat-treated and centrifuged whey permeate (a) 10x (b) 50x*

The two figures above show the thin transparent film that covers the plate. The etching of the stainless steel from sandpapering is visible beneath the fouling.

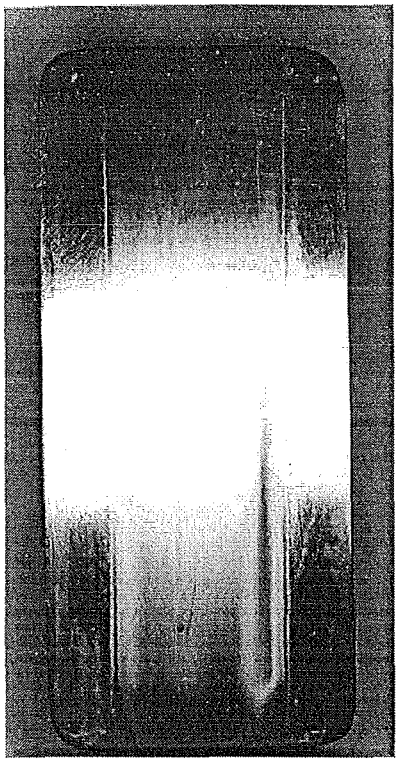

Figure 5.13 Plate fouled with heat-treated and centrifuged whey permeate

5.1.7 Composition of Deposit

The fouling from all samples was analysed on a scanning electron microscope. This allowed basic analysis of the elements present in the deposit (table 5.1).

Table 5.1 *Elemental analysis from scanning electron microscope*

Element	Calcium phosphate	Whey Permeate	Heat-Treated Whey Permeate	Heat-Treated and Centrifuged Whey Permeate
Calcium	19.3%	9.9%	9.1%	1.3%
Phosphorous	14.7%	5.6%	5.0%	1.2%
Potassium	6.5%	2.2%	1.6%	0.8%
Chlorine	6.0%	2.1%	1.4%	0.6%
Iron	1.1%	0.5%	0.5%	53.9%
Chromium	0%	0.2%	0.2%	14.0%
TOTAL	47.6%	20.5%	17.8%	71.8%

The results are presented in terms of elemental percentages, and do not sum to 100% for several reasons. This method of elemental analysis can not detect elements below nitrogen on the periodic table. Elements such as carbon, nitrogen and oxygen are vaporised before they can be detected. Crevices and irregular surfaces on the sample also tend to absorb radiation rather than reflecting it, and contributed towards the low total percentages seen. The large percentage of iron and chromium detected in the last sample show that this method is unsuitable for thin layers of fouling. Obviously the metal surface was being analysed more than the deposit.

The calcium phosphate sample is discussed in section 5.2. Potassium and chlorine are present in this same as potassium orthophosphate and calcium chloride were used to prepare the fouling solution (appendix E).

Samples were also sent for x-ray photoelectric spectroscopy (XPS) analysis. The results are presented in table 5.2 in terms of elemental percentages.

Table 5.2 *Average composition of whey permeate fouling determined by XPS analysis*

	Whey Permeate	Heat-Treated Whey Permeate	Heat-Treated and Centrifuged Whey Permeate
Calcium	4.39	3.89	0.18
Phosphorous	4.63	4.15	0.45
Potassium	0.34	0.34	0.65
Chlorine	0	0	1.03
Sodium	1.21	1.08	1.75
Carbon	51.30	55.00	76.58
Oxygen	30.83	31.19	13.51
Nitrogen	7.31	4.35	6.29
TOTAL	100	100	100.4

It can be seen that the amount of calcium and phosphorous detected is well below that seen using SEM analysis. This may be due to XPS only determining composition on the very surface of the deposit, while SEM analysis tends to detect elements below the surface as well. This characteristic of XPS analysis can be an advantage when the surface of the sample is progressively chipped off using an ion beam. This allows analysis of composition through the thickness of the samples (figure 5.14).

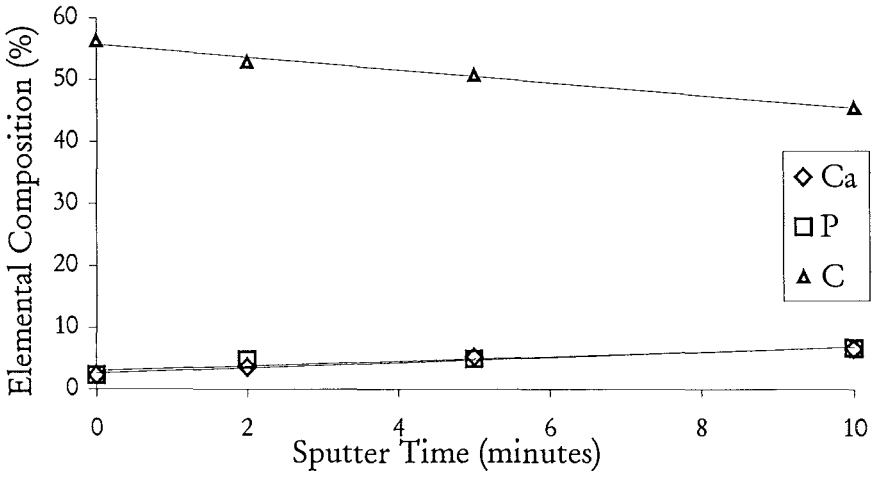

Figure 5.14 *Composition of whey permeate fouling*

At first glance these results would tend to indicate that calcium and phosphorous are only minor constituents in whey permeate fouling. However it must be considered that only the first few Angstroms of the sample are being analysed. Since SEM analysis revealed that these two elements are important components in the deposit, it seems probable that they are concentrated near the metal interface. This is supported by the results above which show that calcium and phosphorous concentrations increase inside the deposit. These results duplicate the findings of Tissier & Lalande (1986b), who also found high concentrations of minerals using an SEM but found only traces when using XPS analysis. Physical examination of the texture of the sample also indicated that it was of a mineral nature, rather than organic.

5.1.8 Scanning Electron Microscope

Figure 5.15 shows that fouling is present even in the heavily pretreated sample fouling. Figure 5.15(b) shows how small crystals are present, from the elemental analysis it can be presumed that this is probably calcium phosphate. The fouling layer was so thin that an acceleration voltage of 2 kV rather was used, rather than the 20 kV used for the other samples. At 20 kV only the surface of the metal was observed and the fouling layer started cracking.

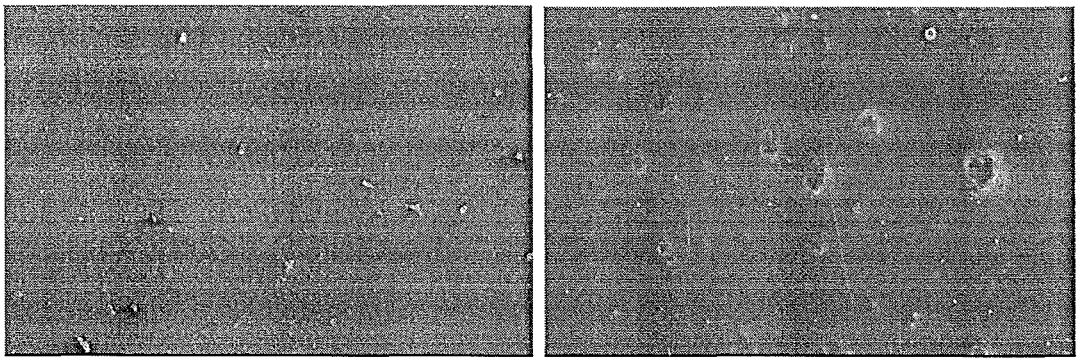

Figure 5.15 *Fouling from centrifuged and heat-treated whey permeate (a) 85x (b) 1,700x*

Figures 5.16 and 5.17 show the fouling present after heat treating at 80°C for 2 minutes but without centrifuging. The structure observed here is assumed to be due to cracking after drying. These pictures were taking with a SEM as described in section 4.3.

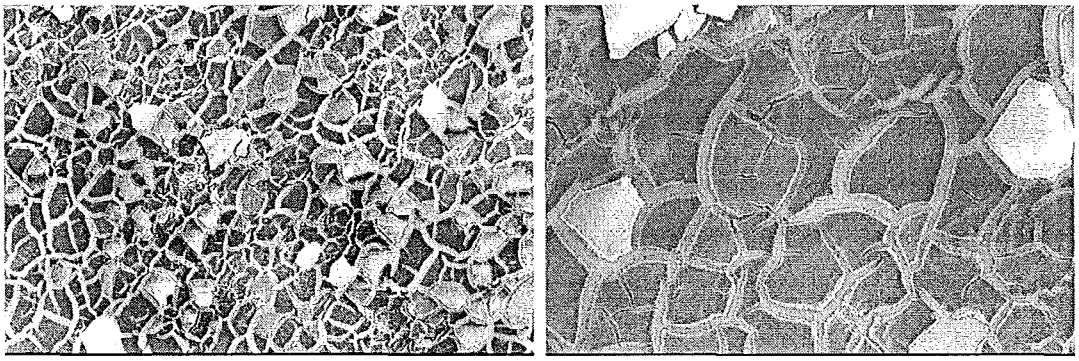

Figure 5.16 *Fouling from heat-treated whey permeate (a) 25x (b) 85x*

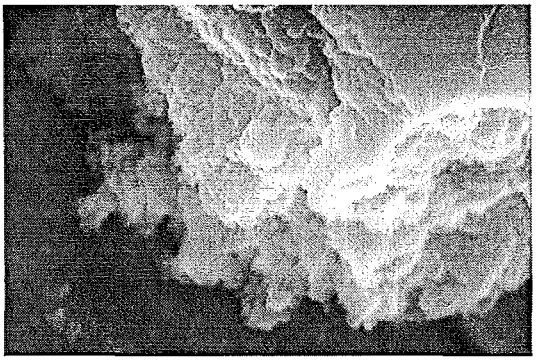

Figure 5.17 *Fouling from heat-treated whey permeate (a) 10,000x*

Figures 5.18 and 5.19 present the fouling caused by untreated whey permeate. It can be seen that the coverage is considerably heavier than whey permeate which was heat-treated and centrifuged (figure 5.15).

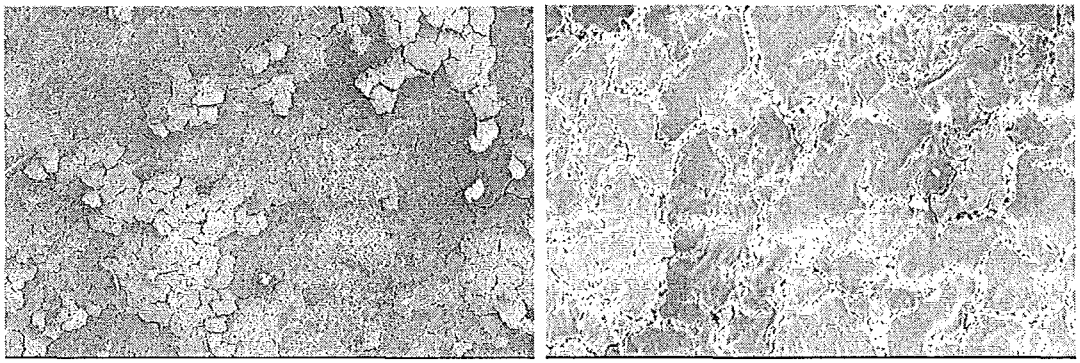

Figure 5.18 *Fouling from untreated whey permeate (a) 25x (b) 85x*

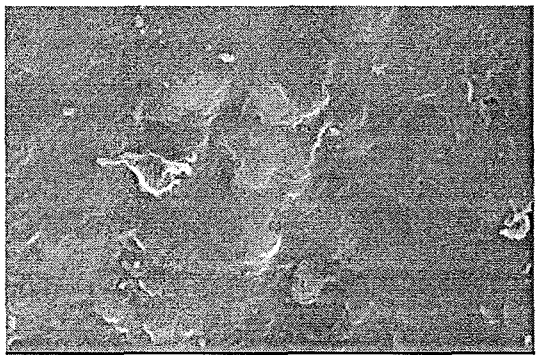

Figure 5.19 *Fouling from untreated whey permeate (a) 10,000x*

5.1.9 Reproducibility of Soiling

To evaluate the repeatability, the experiment was repeated as identically as possible (table 5.3). The product side temperature was 60°C, contact time 1.5 hours, steam side temperature 75°C and the flow rate 340 mL/min.

Table 5.3 *Deposition at standard conditions*

Deposit (g)
0.0435
0.0335
0.0451
0.0370
0.0377
0.0364
0.0339
Average = 0.038
s(n-1) = 0.0045

Taking a 95% confidence interval on these results the error becomes

$$\text{Uncertainty} = \pm \frac{t_{0.025} * s}{\sqrt{n}} \qquad (5.1)$$

Using the data from table 5.3 the error becomes 4.16×10^{-3} g. Dividing this by the average of all seven results

$= 4.16 \times 10^{-3}$ g / 38.2×10^{-3} g

Relative Uncertainty = 11%

The results from this experiment were consistent to within ±11%.

5.2 Calcium Phosphate Fouling

Calcium phosphate solutions were used to analyse the effect of additives (table 5.4). This mineral concentration is representative of that found in whey permeate. It can be seen that a pure whey permeate solution fouls more than the equivalent whey permeate. This is due to non-protein nitrogen stabilisation and is discussed in section 6.7. No pre-treatment was investigated using these solutions.

Table 5.4 *Mass gain by test plate with different fouling solutions*

Solution	Mass Gain (mg/cm^2)
¼ mol/L $CaPO_4$	5.20
¼ mol/L $CaPO_4$ + 0.1% Tetrasodium pyrophosphate	1.87

Addition of pyrophosphate resulted in a finer crystal size and sparser covering of the plate (figure 5.20).

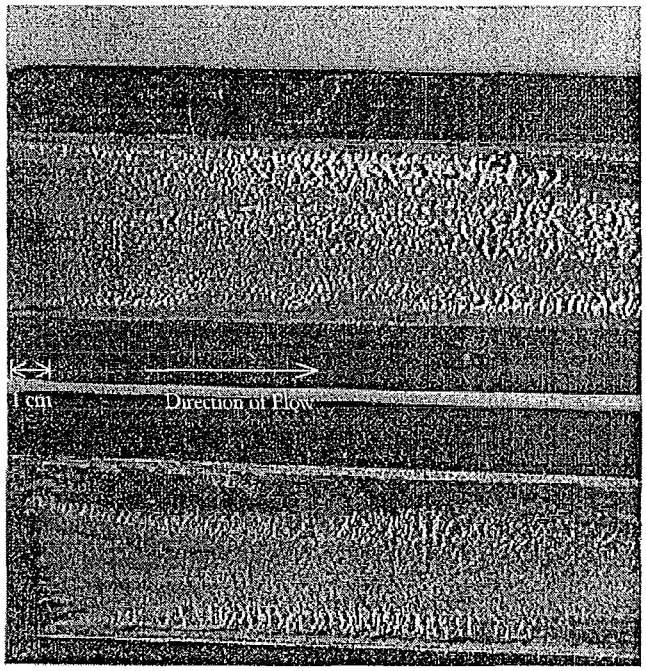

Figure 5.20 *Comparison of calcium phosphate fouling (a) un-inhibited (b) inhibited*

5.2.1 Surface Structure

The fouling from calcium phosphate solutions was studied with an optical microscope. Figures 5.21 to 5.23 show the sparse covering of the metal surface by the fouling layer.

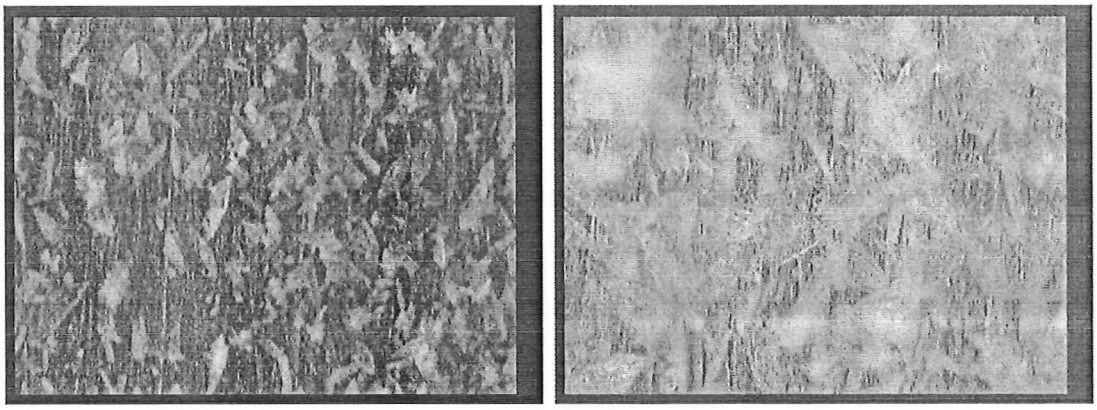

Figure 5.21 *Calcium phosphate fouling (a) 5x (b) 10x*

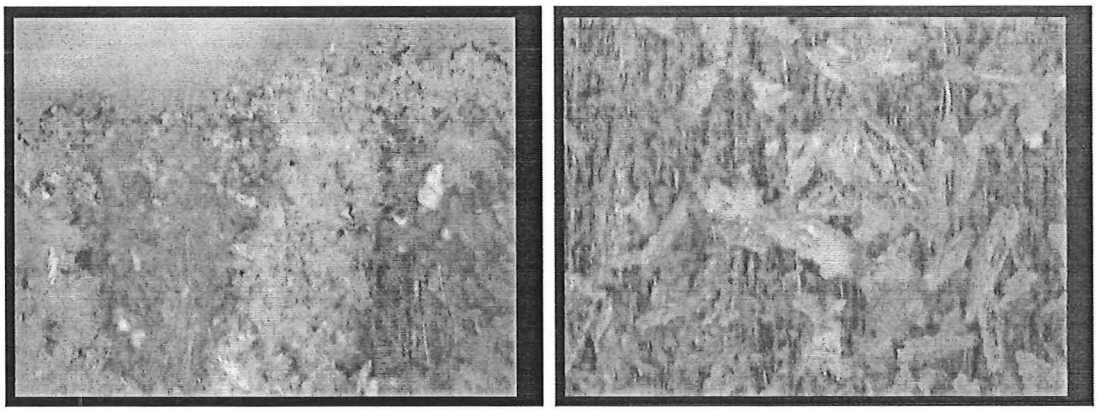

Figure 5.22 *Calcium phosphate fouling (10x) (a) heavily fouled area (b) normally fouled area*

Figure 5.23 Dendritic growth in built up area (50x)

A scanning electron microscope was used to study the surface of the calcium phosphate fouling seen in figure 5.20a. The comparison between calcium phosphate fouling (figures 5.24, 5.25 and 5.26) and whey permeate fouling (figures 5.18 and 5.19) is remarkable. The coverage of calcium phosphate fouling is a lot sparser, and shows definite signs of orderly crystal formation. It is as though the proteins present in whey permeate fouling form some sort of porous layer which the minerals foul onto. This proteinaceous layer provides a high number of nucleation sites and discourages the large crystal growth seen below.

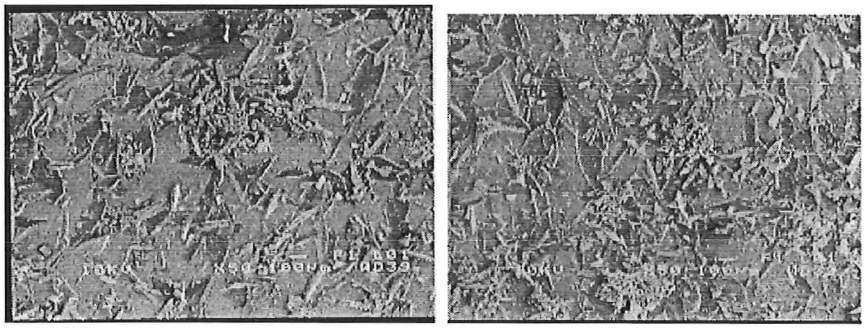

Figure 5.24 *Calcium phosphate fouling (50x)*

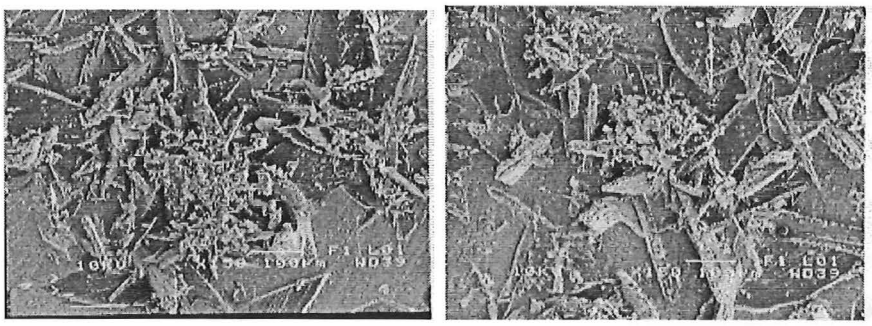

Figure 5.25 *Calcium phosphate fouling (150x)*

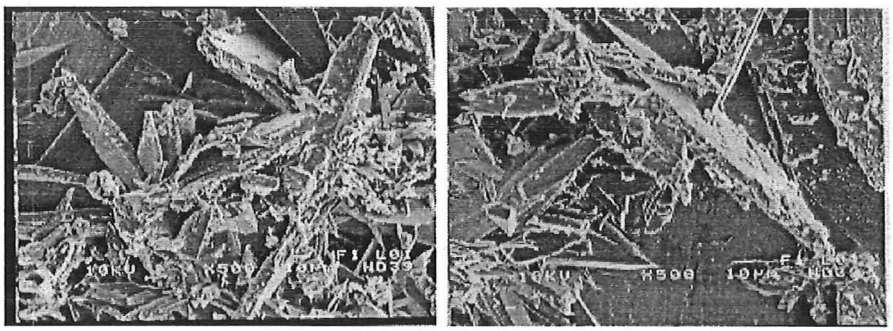

Figure 5.26 *Calcium phosphate fouling (500x)*

6 Discussion

The aim of this research was to examine whey permeate fouling in evaporators and find methods of alleviation. This was accomplished by studying the fouling of two whey permeates and calcium phosphate solutions in an experimental device that mimicked an industrial evaporator.

Several assumptions were made in the design of the apparatus and these are discussed in section 6.1. It was found that whey permeate would not foul below a certain plate temperature, reasons for this are covered in section 6.2. The effects of storage time, preheating and additives are discussed in sections 6.3, 6.4 and 6.5. The effect that evaporator design has on fouling is shown in section 6.6. Section 6.7 deals with the mechanism of calcium phosphate precipitation. The last part of this chapter (section 6.8) makes recommendations which will minimise the fouling problem.

6.1 Experimental Methods

The fouling apparatus presented in chapter 4 was used to investigate the effect of heat treatment and additives. The equipment was operated at conditions which simulated the first effect of a whey permeate evaporator processing 40,000 L/hr. A steam side temperature of 75°C, and a permeate entry temperature of 60°C was used for most experiments. The flow rate per meter of heat transfer area was similar to a full size industrial evaporator (appendix C). Several assumptions were made to simplify the apparatus. It was assumed that the operating pressure would not have a great effect on fouling. It was also assumed that the lack of a large vapour core would have negligible effects. Concentration and flash effects were also ignored.

Industrial evaporators operate below atmospheric pressure. This produces a lower boiling point and allows steam of lesser quality to be used in the operation. A lower processing temperature is also desirable when dealing with dairy products that are heat sensitive. The test rig for this project operated at atmospheric pressure. This will not have an appreciable effect on the fouling of whey permeate, as this is a liquid-solid mechanism. This means that the activation energies of each step in the fouling process are almost pressure independent.

As vapour is generated in an evaporator, it moves downwards through the centre of the tube at high speed. The velocity of these vapours can approach the speed of sound at the bottom of the calandria (Woodshead, 1997). The has a huge shearing effect on the thin layer of water moving

down the inside of the tube walls, and causes it to 'flatten' further. This decreases the film thickness and increases turbulence, which tends to aid heat transfer. It is beneficial in other ways, as it stops 'dry-on' by ensuring the liquid is evenly spread over the entire surface of the tube (Billet, 1989). It was decided to not include a method of simulating this in the fouling apparatus, as it would have added a great deal of complexity. The film thickness will have minimal effect on the fouling properties of a solution. The increase in turbulence from the vapour shear will have an effect on the mass transfer boundary layer. However, this project was aimed at providing a comparative measure of fouling under different conditions. This lack of a vapour core with not hinder comparison of fouling alleviation measures.

As the fluid travels down the length of the evaporator, it evaporates and becomes more concentrated. This effect could not be modelled, as the plate length used was only 130 mm, not the 10 m found in industry. This will not have a large effect, as fouling mainly consists of calcium phosphate. This mineral precipitates due to becoming super-saturated by heating. Even before heating, when sitting at room temperature, the solution is saturated by an order of magnitude (section 2.4). Therefore the ~5% increase in concentration that can be found in a single evaporator tube is insignificant compared to the amount of super-saturation that already exists.

A typical operating pressure for the first effect of the Scheffier evaporator is around 40 kPa, which gives a boiling point of approximately 78°C. The preheater to this effect heats the entering fluid to temperatures in excess of 80°C. This means that when the whey permeate first enters the evaporator chamber it is superheated, and some of it instantaneously flashes into vapour. Since the flash causes no heating, and the increase in concentration is negligible, it is unlikely that it would cause any fouling. This is supported by the observations of operators at lactose, who have observed that no fouling occurs on or above the distribution plates (Woodshead, 1997). For this reason the experimental apparatus was not designed to imitate flash effects.

6.2 Critical Fouling Temperature

The results shown in figure 5.4 indicate that there is a temperature below which whey permeate will not foul in the experimental rig. This appears to be approximately 60°C. Note that this is not a true indication of what would happen in an industrial evaporator, as a longer exposure to the temperature may cause some precipitation. What this does indicate however, is the sensitivity of the fouling mechanism to heat. This is very useful in predicting the extent of preheating required to provide some relief from fouling.

This temperature where the onset of fouling occurs is clear for several reasons. As the fouling process is kinetic, the time of exposure is important. The calcium phosphate in raw whey permeate is in solution or combined with the various non-protein nitrogen (NPN) available. Any calcium which is combined with NPN has a lower activity than that in solution. This means that whey permeate can support a larger proportion of calcium phosphate than the solubility product indicates. This solution is only meta-stable in that over time some of the calcium phosphate will separate itself from the protein and migrate into the liquid bulk. This will raise the concentration in solution and cause precipitation. Once the calcium phosphate is in solid form it will never redissolve, because the solubility constant is so low that the transformation can be considered irreversible. See section 6.7 for a full discussion on this effect.

The effect can be seen when the solution is heated. The protein fragments and other nitrogen sources start to lose what ever quaternary structure they may have. This means that the calcium and phosphate ions that were 'sheltering' in the folds of the protein are suddenly ejected in the bulk, raising the concentration there. At the same time, the calcium phosphate becomes less stable because of its reverse solubility properties. This combination of effects cause the exponential increase in fouling as shown in figure 5.4, as temperatures above 60°C cause rapid protein denaturation (de Jong *et al.*, 1994). This means that the unstable calcium phosphate has 'no where to hide' and must precipitate in bulk. This is the crux of the fouling problems in the primary evaporators at Lactose New Zealand.

The preheating times in this research were chosen after considering these results. Since the whey permeate samples were heated in stainless steel beakers rather than a heat exchanger, the heating time was quite appreciable. When heating in a 80°C water bath, it took approximately one minute to reach a temperature of 50°C. Since this is the temperature at which proteins are irreversibly changed (de Wit & Klarenbeek, 1984; Hegg *et al.*, 1985; Jelen & Rattray, 1995), the first minute of heating was not included in the total time. A typical time/temperature profile for this preheating is shown in figure 6.1.

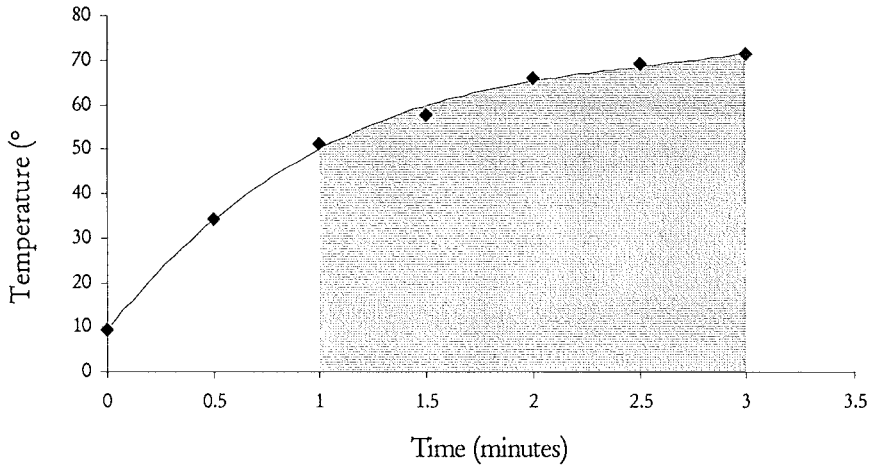

Figure 6.1 *Temperature profile for preheat treatment*

It is important to note that there was no heavy fouling in the stainless steel beakers used for heating, even if there was precipitation in the bulk of the solution. This can be attributed to the high level of agitation in the beakers, provided by a glass stirring rod. This meant that T_{wall} was close to T_{bulk}. A very slight slimy film was noticed on the beaker walls after processing at high temperatures. From the texture, this appeared to be a very faint proteinacous layer. This layer was not investigated further as it was minor. Unfortunately this very minor fouling is probably not representative of what will occur in an industrial operation as very small volumes were processed in the laboratory investigation. However, even if the preheat does experience fouling this will be still be effective in reducing the deposit formation in the evaporator. The preheat equipment will be small, easy to clean and two can be run in parallel to guarantee continuous operation. In this case moving the fouling point upstream to a 'sacrificial' piece of equipment would be very beneficial.

Industrially, DSI (direct steam injection) heating might be considered. This has the advantage of no heat transfer surface being in contact with the solution. However Burton (1968) mentions that direct heating methods still suffer from fouling, due to supersaturated solution being carried

towards the enclosing surfaces of the DSI. Deposition then occurs as if these surfaces were heated. This was also noticed in this research. During processing of whey permeate, fouling occurred after the test plate on the perspex walls of the apparatus, even though no heating took place at this point. This is due to the kinetic nature of the fouling process. Calcium phosphate which is not given enough energy to nucleate homogenously, may do so heterogeneously on metal surfaces. Likewise, proteinacous material which is denatured can adsorb to a surface some distance downstream from where it was heated. A DSI heater will experience fouling even though there is no surface in direct contact with the product, but deposition will be much lighter than traditional heat treatment methods.

6.3 Storage Time

A very significant trend is the increase in fouling observed when whey permeate is stored. This conflicts with reports from operators that indicated storage time decreased fouling (Woodshead, 1997). In fact, both of these observations are correct. In the short term calcium phosphate tends to precipitate via the mechanism covered in section 6.7. This fine solid can then stay in suspension for long periods of time. When this whey permeate is later processed, the suspended calcium phosphate is free to bond onto the stainless steel surface during heating and cause fouling. In the experimental rig, the processed fluid is only exposed to the heat transfer area for a few seconds. Since precipitation is a kinetic process, some of the calcium phosphate that was supersaturated will not have time to remove itself from solution. However, already precipitated calcium phosphate does not have this limitation and is free to bond immediately. Therefore, precipitation before processing leads to high fouling levels.

In the long term, the same process is occurring. Calcium phosphate is precipitating and becomes suspended in solution. However, over long periods of time (~2 weeks) the precipitate has time to settle. This means that calcium phosphate ends up on the bottom of storage silos and tankers, rather than inside evaporators. This was clearly seen in solutions held for extended periods in the laboratory. Even when the whey permeate had been preserved with the addition of thymol, white flocculant would appear after approximately a week. Whey permeate processed after this long period did not observably foul.

Looking at the situation practically, it is not possible to hold the million of litres of whey permeate that arrive each day for enough time to precipitate all the calcium phosphate present. Holding in

the short term increases the fouling problem. Therefore, whey permeate should be processed as quickly as possible. The suppliers of whey permeate (e.g., Kiwi Dairies Ltd) should also be contacted and encouraged to send their whey permeate to the LNZ site as soon after processing as possible.

6.4 Preheating

The most important result from this project is the effect of preheating on evaporator fouling. It can be seen from figure 5.6 that preheating at 80°C, then centrifuging before processing leads to a drastic reduction in fouling. This is a caused by a combination of factors.

Heating the feed causes calcium phosphate to become even more super-saturated than it was initially. At the same time, the nitrogen sources that are available are being denatured. This leads to the loss of structure proposed in section 6.7. This large scale precipitation means that calcium phosphate is not available for fouling in the evaporator. The denaturation of the NPN also has an important effect. Many workers have proposed protein as the initial fouling layer (Gotham *et al.*, 1992; Fryer & Belmar-Beiny, 1991; Tissier & Lalande, 1986). Denaturing these in a preheater causes them agglomerate and have less active sites for bonding to the stainless steel walls.

This method also has an advantage over the use of additives. It has been reported that higher levels of minerals make it difficult to crystallise lactose (Thomas, 1998). The addition of pryophosphates may avoid fouling in the short term, but may cause problems further downstream. For this reason it appears wise to remove calcium phosphate from the feed stream if possible.

Although precipitation occurs during storage, much coarser solids are formed during heating. These tend to settle much more quickly than fine precipitates formed over a long time period. This is why heat treatment without centrifuging provides some relief from fouling - although it is more effective when used with centrifuging. Some of the calcium phosphate that forms tends to settle and not be available for later fouling. The precipitate that does not settle in time has less surface area to adsorb to the stainless steel with. However, coarse fouling of the heat transfer surface still occurs.

A major concern about the introduction of this process is the effect of pH. Brothersen *et al.* (1982) & Rao (1994) showed that heating milk permeate to 80°C at pH 6.6 resulted in removal of 40% of

the calcium. The same treatment at pH 6.2 only removed 16% of the calcium and at pH 6.0 no precipitation occurred. Fortunately whey permeate contains less proteins than milk permeate, and therefore the stability of the milk salts is much lower (Schmidt & Both, 1987). The whey permeate used in this experimentation had a pH of 5.6 and still exhibited a precipitation. It would be useful however to monitor the pH of permeates and the precipitation they exhibit so that the pre-treatment process can be optimised.

From the results presented in section 5.1.5 it is clear that heat treatment by itself is not a highly effective method of reducing fouling. The precipitate that forms during the pretreatment process is free to deposit in the evaporation process if it is not removed. That is why the centrifuging process was developed. This is discussed in terms of the fouling mechanism in section 6.7.

6.5 Use of Additives

The effect of additives on fouling was studied briefly. Prices provided by J.C. Sherratt & Co Ltd (Christchurch, New Zealand) indicate that additives would be an expensive option compared to heat treatment. BUDIT 7 H is a linear long chain polyphosphate with an average chain length of seven. This has been priced at between $2.90 to $3.40 per kg. To alleviate fouling between 0.1% to 0.2% based on dry weight must be added. This would add a cost of up to $16.32 per tonne of lactose (appendix H). Assuming that the additives give evaporator run times equal to that experienced by whole and skim milk processors (14 hours), and that evaporation is a bottleneck in the process, it is estimated that $257,000 would be saved each year by their use. However, addition of polyphosphates to the process has several significant problems.

Using this method the calcium phosphate that would normally be deposited in the evaporation stage, will stay in the process. This will cause problems with lactose crystallisation and also lower product quality as it is difficult to remove with washing. Polyphosphate would also have to be declared to consumers as a product additive. If all of it could be removed by washing, it could be considered a processing aid, but this is unlikely to happen. Any such addition would tarnish the imagine of New Zealand lactose being 'clean and green' and is undesirable. It is therefore not recommended that this process be implemented.

6.6 Evaporator Design

The existing distribution plate of the industrial evaporators studied lacked vapour downcomers. These are short lengths of tube which pass through the distribution plate and allow vapour created by flashing to escape without having to pass though the distribution holes. The top of the tubes are 30-40 mm above the top of the plate, which is above the liquid level. Vapour downcomers are needed to avoid buildup of pressure in the evaporator head, which leads to dry-on as described in section 3.3.

It is easy to add these devices to existing distribution plates for a trivial cost. For an evaporator processing 40,000 L/hr of whey permeate, it was calculated that the first effect should have 12 vapour downcomers of 51 mm (2 inch) internal diameter (Appendix F). The fittings described should be added to the first effect of an existing evaporator, where the flash is most significant. This configuration is now standard for newly built evaporators, and is recognised as a method of reducing fouling.

6.7 Fouling Mechanism

After considering the effects of heat treatment, storage and polyphosphate inhibition, the following model was developed (figure 6.2).

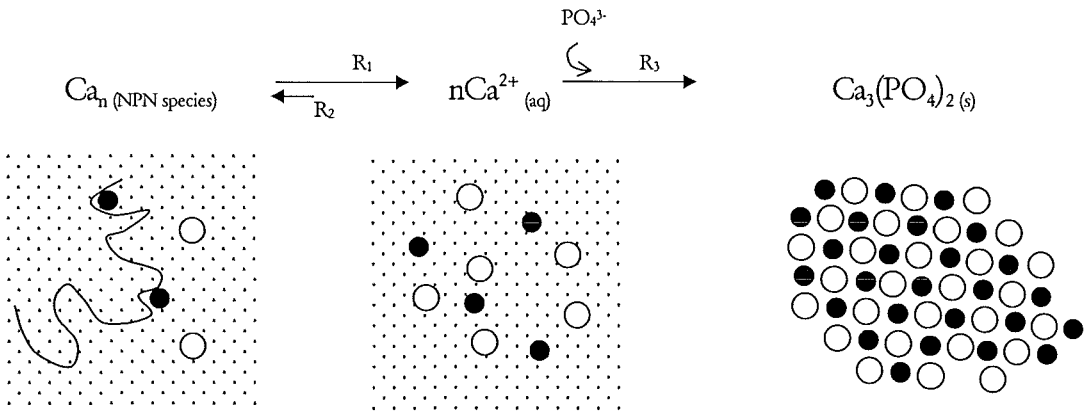

Figure 6.2 *Distribution of calcium phosphate in whey permeate (●represents a calcium ion, ○ represents a phosphate ion, · represents a water molecule)*

Where R_1 is a function of:

a) Rate of decay of NPN-species (oxidation, acidity, enzymes and heat denaturation)

b) Natural dissociation (time, temperature, acidity and pH)

And R_3 is a function of:

c) $[Ca^{2+}]$, $[PO_4^{3-}]$, K_{sp}, pH and temperature

d) Number of nucleation sites available

The rate constant R_2 represents the reabsorption of ionic calcium into non-protein nitrogen species. When considering heat treatment and storage effects it can be assumed that this term is negligible as the NPN is irreversibly denatured. Note that the precipitation of aqueous calcium phosphate into a solid form is assumed to be an irreversible process. Since the solubility product (K_{sp}) of calcium phosphate is so low (4.7×10^{-59} mol/L for hydroxyapatite), the driving force for dissolving is very low in any practical situation. This means the rate constant for the redissolving of calcium phosphate can be neglected. It is important to remember that NPN in this model refers to some components that could be considered proteins and their behaviour reflects this. This is discussed in section 3.0.

When whey permeate first enters the lactose production process a majority of the calcium phosphate is associated with the NPN species present. Since the size of NPN is small, these ions are neither in a micelle (as formed by casein protein) or in solution. They have an activity somewhere in between. Even though the NPN is only about 10% of the solids in whey permeate, it is vital in calcium stabilisation. This can be seen in the level of total calcium present in the whey permeate, which is well in excess of the solubility product, and yet precipitation occurs very slowly. NPN stabilises the calcium. This association is not surprising when it is considered that 77% of the calcium in milk is supported within the casein micelle (Sandu & Lung, 1985).

Precipitation does occur when a calcium ion liberates itself from the NPN, and enters the aqueous solution. The calcium sometimes leaves the influence of the NPN due to localised saturation on one part of the protein or because the NPN itself is being broken down by proteolytic enzymes in the milk (de Jong *et al.*, 1998). This causes the solubility product to be exceeded and if nucleation sites are available a calcium phosphate crystal will form. If precipitation must occur homogenously (e.g., no surfaces or impurities are present), then the saturation point may be greatly exceeded without crystallisation occurring. Once solid calcium phosphate does form however, it will not realistically redissolve at the pH of normal whey permeate, and the reaction can be considered irreversible.

This model accounts for several effects found in this research. The usefulness of preheating in reducing fouling can be explained by looking at the first half of this mechanism. Heating at 80°C tends to denature the NPN species present, and make them lose their quaternary structure. This lowers their ability to stabilise other species, and releases large amounts of calcium ions into solution. At the same time the reverse solubility of calcium phosphate means that less mineral is soluble, so precipitation occurs (Davies & White, 1959). If a direct steam injector is used, precipitation will mostly occur homogenously.

This research clearly shows that preheating by itself will not greatly reduce fouling. The calcium phosphate that is precipitated must be removed or it will adsorb to the heating surface during evaporation. This indicates that solid calcium phosphate bonds in some way which is not related to the precipitation mechanism. Since this deposition involves large particle sizes (~0.5 mm), proteins probably do not catalyse this reaction. It is likely that the precipitate adsorbs when it passes close to the thermal boundary layer where the temperature is high. This may precipitate calcium phosphate that is still in solution and close to the particle, and act as a bridge between the solid calcium phosphate and the metal surface.

Since the calcium ions are only partially associated with the NPN, over time some of them 'leach' out to enter the solution. As mentioned above, this results in slow precipitation. This explains the trend whereby whey permeate held for long periods fouls less, as less calcium phosphate is available to precipitate.

Polyphosphate additives probably work by inhibiting the precipitation part of the mechanism. They precipitate in place of a phosphate ion and 'close down' an active site. This is described in section 2.4.3.

The lack of induction time observed when evaporating whey permeate can also be explained in terms of this model. When processing whey permeate, the heat transfer area is almost immediately covered by a very thin transparent white film. Within 90 seconds this is observable by the appearance of an interference film on the plate. This was previously observed by Schraml *et al.* (1996). Optical and scanning electron microscope examination of this deposit showed that it consisted mainly of protein, with widely spaced small calcium phosphate crystals. It would appear that the NPN species present are very quick to foul and are not hindered by having to form an orderly crystal structure as calcium phosphate. Proteinacous compounds therefore are able to form

an early layer, while the minerals in the solution are still depositing via dendritic growth. Considering the evidence presented here, it appears that proteins adsorb first, but do not necessarily catalyse the deposition process. Calcium phosphate then precipitates and forms a level of high concentration near the hot metal surface where it is most supersaturated. This can occur because the protein structure is voluminous and open (Burton, 1968).

The difference observed in the fouling between Kiwi Dairies and Anchor Products Hautapu whey permeate may be due to the contrasting ultrafiltration methods that both sites use. Hautapu uses a traditional ultrafiltration method which processes whey at 50°C, while Kiwi uses a new cold ultrafiltration method which processes product below 10°C. By looking at the second half of the model above, it can be seen that using the warmer temperature will tend to shift the equilibrium to the right. This precipitates calcium phosphate and contributes towards membrane fouling, but does make the fluid easier to evaporate later. The Kiwi process keeps the feed cold, and more of the minerals remain with the protein in solution. This allows more efficient WPC production, but makes lactose production difficult.

6.8 Recommendations

Several changes can be made to Lactose New Zealand's current processing and cleaning regimes that would decrease the fouling problem. The addition of vapour downcomers was discussed in section 6.6. Another equipment addition should be a preheater just before the first effect of the primary evaporators (appendix A).

This equipment would allow the temperature of the feed to be raised to 80°C and then held for two minutes. The feed would then be passed through a clarifying centrifuge and the calcium phosphate precipitate separated. Whey permeate that was passed through this process deposited only 6% of the mineral that untreated product did. In studying the economics of the situation, it was assumed that this reduction in fouling would be enough to provide 14 hours of operation between cleanings. This is generally the length of time that a milk evaporator would be expected to run before cleaning. During whey permeate evaporation, run times as short as 4 hours have been experienced, although 6-8 hours is average (Woodshead, 1997).

Two options for preheat-treatment were considered. The first used a direct steam injection (DSI) system to heat the product, the second used a conventional heat exchanger for heating. While both

methods will cost approximately $480,000 (appendix A) the DSI option has the advantage of no direct surface being in contact with the product, and therefore less fouling. However, culinary quality steam must be used, as the heating medium will mix with the product. The indirect heating option will experience more fouling and is slightly less energy efficient, but can use non-food grade steam.

After heating the product is held in an insulated stirred tank. The average hold up time in this vessel is two minutes. This is followed by separation of the calcium phosphate precipitate by using a clarifying centrifuge. This removes the solids as a sludge with water. This waste product will contain mainly calcium phosphate and some protein components. There will also be lactose losses in this part of the process, but they will be minor as the lactose will be in solution at this point and not affected by gravity separation. The only lactose removal will occur with the liquid in the sludge and this will be small. Any lactose crystals that have formed during transportation will be dissolved by the 80°C/2 min treatment. Qualitative laboratory trials showed that the precipitate formed contained solids that were water insoluble but dissolved in acid. This indicates that the solid was mainly mineral.

The product from this process can be directly fed into the first effect of the evaporators. With the removal of a majority of the calcium phosphate longer running time and less fouling will be observed.

After analysing the savings that these systems would make, it was found that the payback period for this equipment would be 1.8 years. This value is a rough approximation as it was made assuming a marginal profit of $100 per tonne of lactose. The marginal profit/ton is commercially sensitive information and can not be estimated more accurately. The economic analysis and design of both options is shown in appendix A.

7 Processing Recommendations

- 12 vapour downcomers of 2 inch internal diameter should be added to the first effect of the existing Lactose New Zealand evaporators (section 6.6, appendix F).

- The pH of Kiwi RO entering the plant should be monitored. pH should then be correlated with precipitation of calcium phosphate under the preheating conditions described in section 6.4.

- A preheating (80°C for 2 minutes) and centrifuging process should added as described in section 6.8 and appendix A.

- Whey permeate should be processed as soon as possible to reduce fouling caused by storage time. Suppliers should be contacted and asked to minimise their storage time (section 6.3).

8 Conclusions

- Preheating and then centrifuging is an effective method of alleviating fouling. Preheating at 80°C for 2 minutes, then centrifuging at 630 g for 3 minutes reduced fouling by 94% at conditions simulating LNZ's evaporators.

- Preheating at 80°C for 2 minutes without centrifuging will only reduce fouling by 39%.

- Storage time increases fouling in the short term, but reduces fouling when over ~2 weeks.

- Additives are effective at reducing fouling but may cause crystallisation problems downstream from the evaporation stage.

- Nanofiltration, ion exchange and electrodialysis can provide some relief from fouling. The capital cost of these methods is prohibitive when producing a low cost product such as lactose powder.

- Non-protein nitrogen species in whey permeate are important in calcium phosphate stabilisation. Denatured NPN does not stabilise minerals.

- Minerals exist in whey permeate in a mixture of three phases, suspended as a solid, in solution and associated with NPN. Over time the minerals tend to migrate from the NPN phase to the solid phase.

- Part of the present fouling problem is due to the poor distributor plate design of LNZ's evaporators. This can be solved by the addition of vapour downcomers.

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Appendix A - Design of the Preheating Process

Two methods were analysed for the heat-treatment of whey permeate. The first method used a direct steam injector (DSI) to provide heat, the second used a heat exchanger. Costs for both designs are similar ($400,000), but the DSI method has the advantage of less fouling occurring. Direct steam injection would require culinary quality steam however and is based on an existing UHT design (Hinricks & Kessler, 1995). Both options are shown in figure A.1.

Economic Analysis - Capital Costs

Both options were costed using the Lang factor method as described by Jebson & Fincham (1994). Much of the information in this source was taken from Ulrich (1984). All costings are in NZ dollars at June 1998 (table A.1)

Table A.1 *Equipment Cost*

Equipment	Option One	Option Two
Direct Steam Injection Unit	5,000	N/A
Heat Exchanger	N/A	3,000
Holding Tank	10,000	10,000
Pump	17,600	17,600
Centrifuge	374,000	374,000
Total	**406,600**	**402,600**

It can be seen that both options will have an almost identical cost. It was assumed that the equipment and instillation for both methods will cost around NZ$405,000. This was multiplied by 1.18 for the contingency and contractors fee (Ulrich, 1984).

Total Cost = $405,000 x 1.18

= $477,900

say a total cost of: = **$480,000**

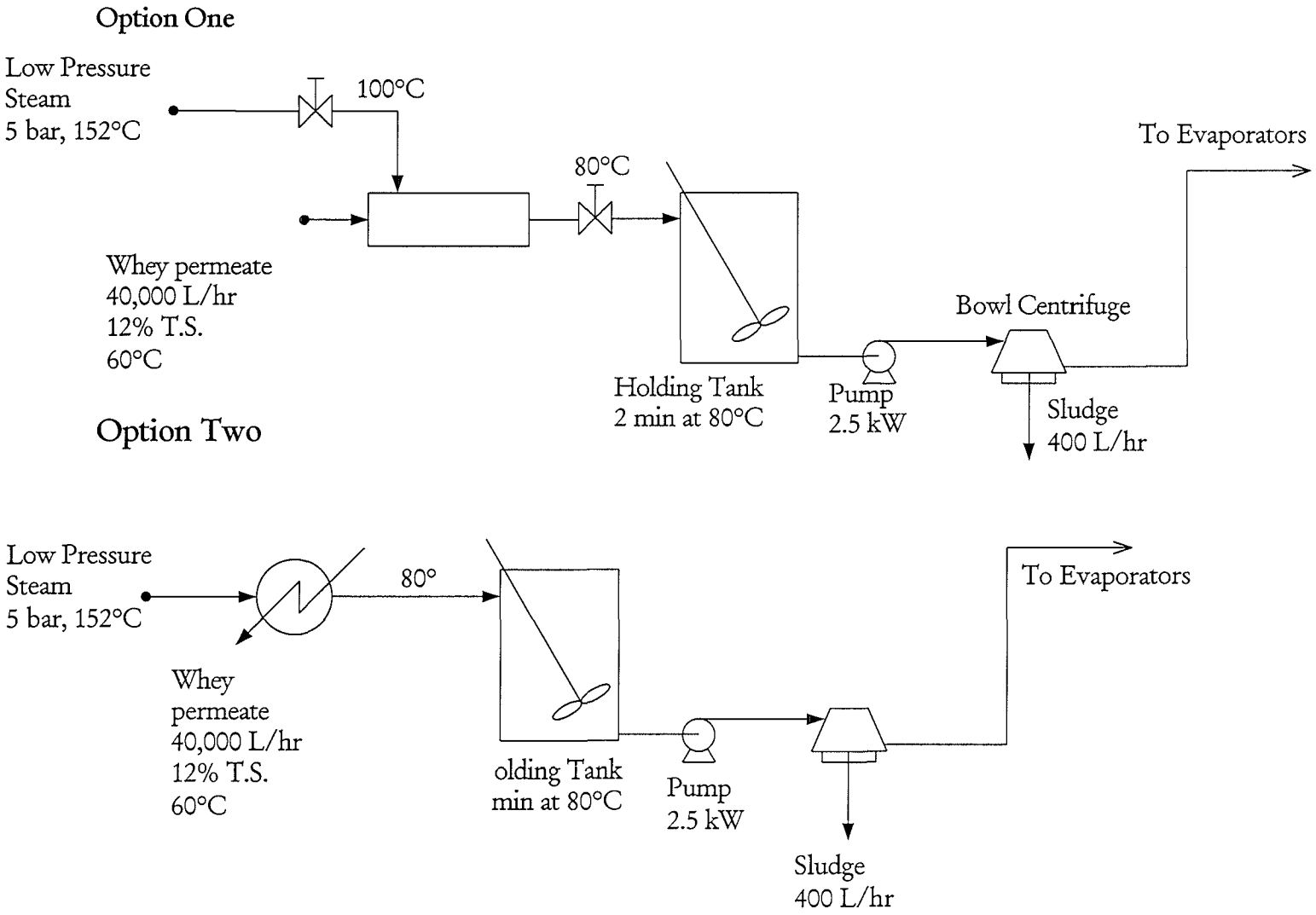


Figure A.1 *Options for preheating design*

Example Economic Analysis

This example economic analysis assumes that reducing fouling in the primary evaporation stage of lactose production will allow runtimes close to those achieved in the treatment of whole or skim milk to be reached. This is in the region of 14 hours between cleanings. An average run time while processing heavily fouling substances, is between 6-8 hours. An average of 7 hours for untreated Kiwi RO whey permeate was assumed. The costs and revenue used in this calculation need to be revised with accurate company data.

Assuming that the evaporators run for 34 weeks a year (Styles, 1998):

34 weeks x 7 days x 24 hours = 5,710 hours / year

Untreated whey permeate:

7 hours processing + 2 hours cleaning = 2/9

Treated whey permeate:

14 hours processing + 2 hours cleaning = 2/16

Multiply the above fractions by 5,710 processing hours the amount of time spent on cleaning is found:

2/9 x 5,710 = 1,269 hours on cleaning

2/16 x 5,710 = 714 hours on cleaning

A clean uses about 70 L of 70% nitric acid per hour, which is diluted down to ~2%. At a cost of $1.30 / L (CCL, New Zealand).

Untreated: 88,830 L/year x $1.30 / L = $115,500

Treated: 49,960 L/year x $1.30 / L = $65,000

This is a CIP saving of **$50,500 /year**

Less time spent cleaning means more time processing product. The primary evaporation stage can sometimes be a bottleneck in the process and limit total production. If this is not the case, this

section of the economics should be adjusted. Since the plant processes 40,000 L of 10% lactose per hour, each hour of extra processing time increases total production by:

40,000 L/hr x 10% lactose = 4 ton lactose /hour

After treatment:

1,270 - 714 = ~560 hours / year

560 extra hours will be available. Assuming that the marginal profit for a ton lactose is $100.

560 hours x 4 ton/hour x $100 /ton = $222,400

The increase in marginal profit: = **$222,400 / year**

The major running cost is the steam needed to heat the product to 80°C. Since the majority of this heating will be done with recompressed steam from the evaporators, the cost will be minimal. The only extra heat needed will be to heat the input flow above the boiling point of the first evaporator (78°C). It is estimated that only about 4°C of heating will be required (Styles, 1998). For a flow rate of 40,000 L/hr:

$40{,}000 \text{ kg/hr} * (h_{(80°C)} - h_{(76°C)})$

40,000 kg/hr * (391.6 kJ/hr - 388.7 kJ/hr) = 116,000 kJ/hr

If this is provided by direct injection of steam at 10 bar, the amount needed is:

$116{,}000 \text{ kJ/hr} / h_{(fg,\ 10\ bar)}$

116,000 kJ/hr / 2,258 kJ/kg = 51 kg steam/hour

At a cost of $13.20 / ton this becomes:

0.051 ton/hour * $13.20 /ton = $0.68

Over one year (5,710 hours) this becomes:

$3,870 /year

Table A.2 *Savings after installation*

Savings	$NZ	Costs	$NZ
Less chemicals used in CIP	$50,500	Steam	$3,870
Increase in marginal profit	$222,400		
Total	**$272,900**		**$3,870**
Total Savings			**$269,000**

Payback Period

From the capital analysis we can see that it will cost $480,000 to install either option. Therefore it will take 1.8 years to pay back the initial investment.

Appendix B - Fouling Test Cell Drawings

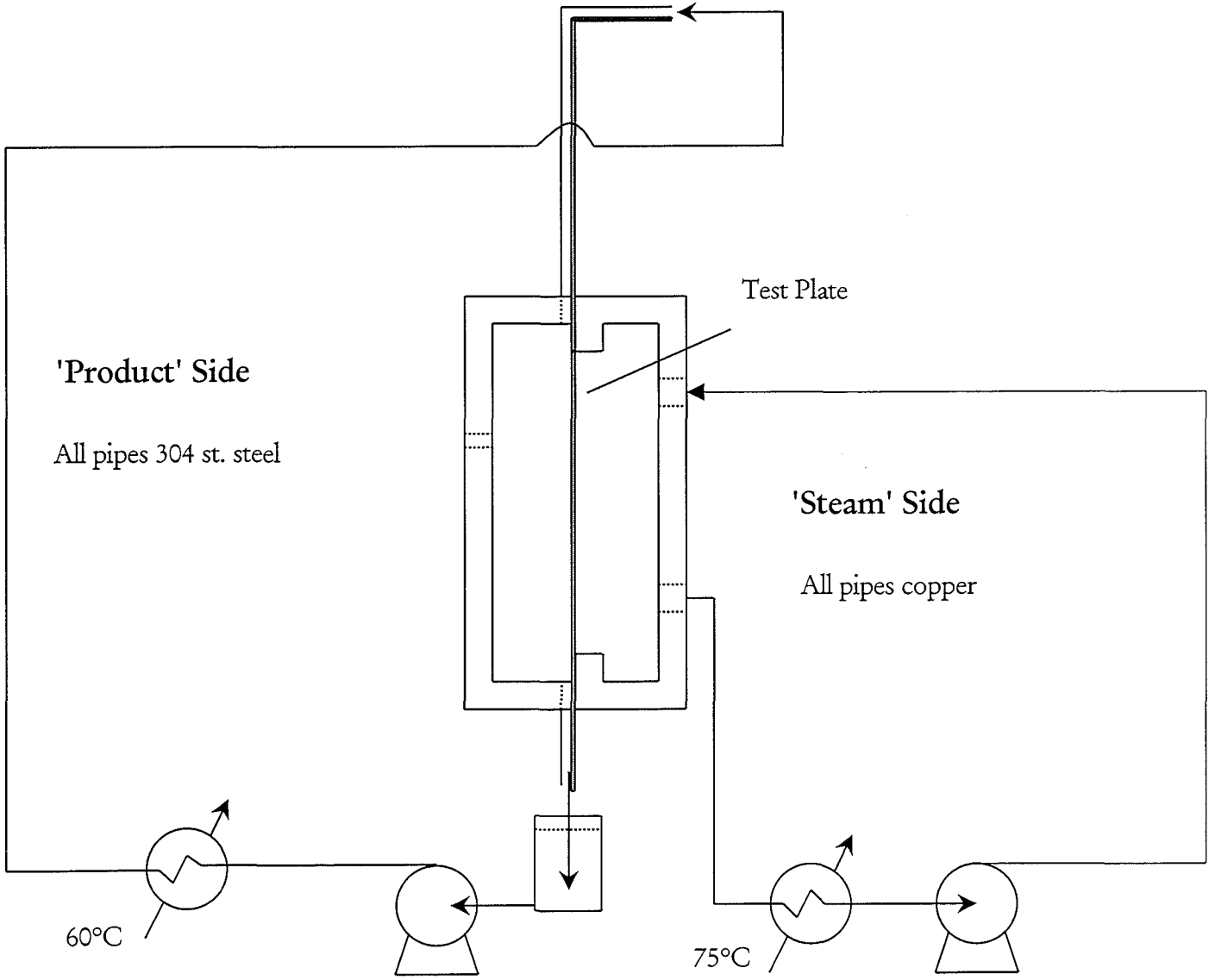
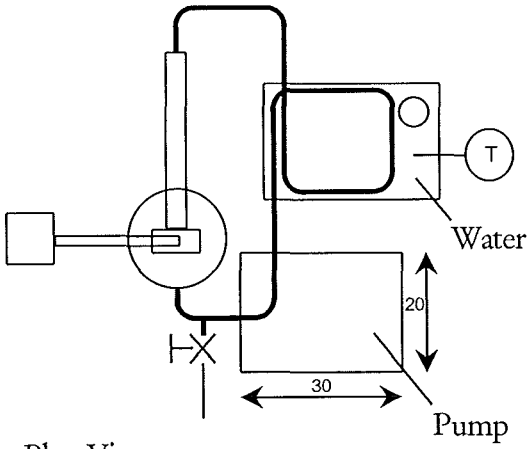
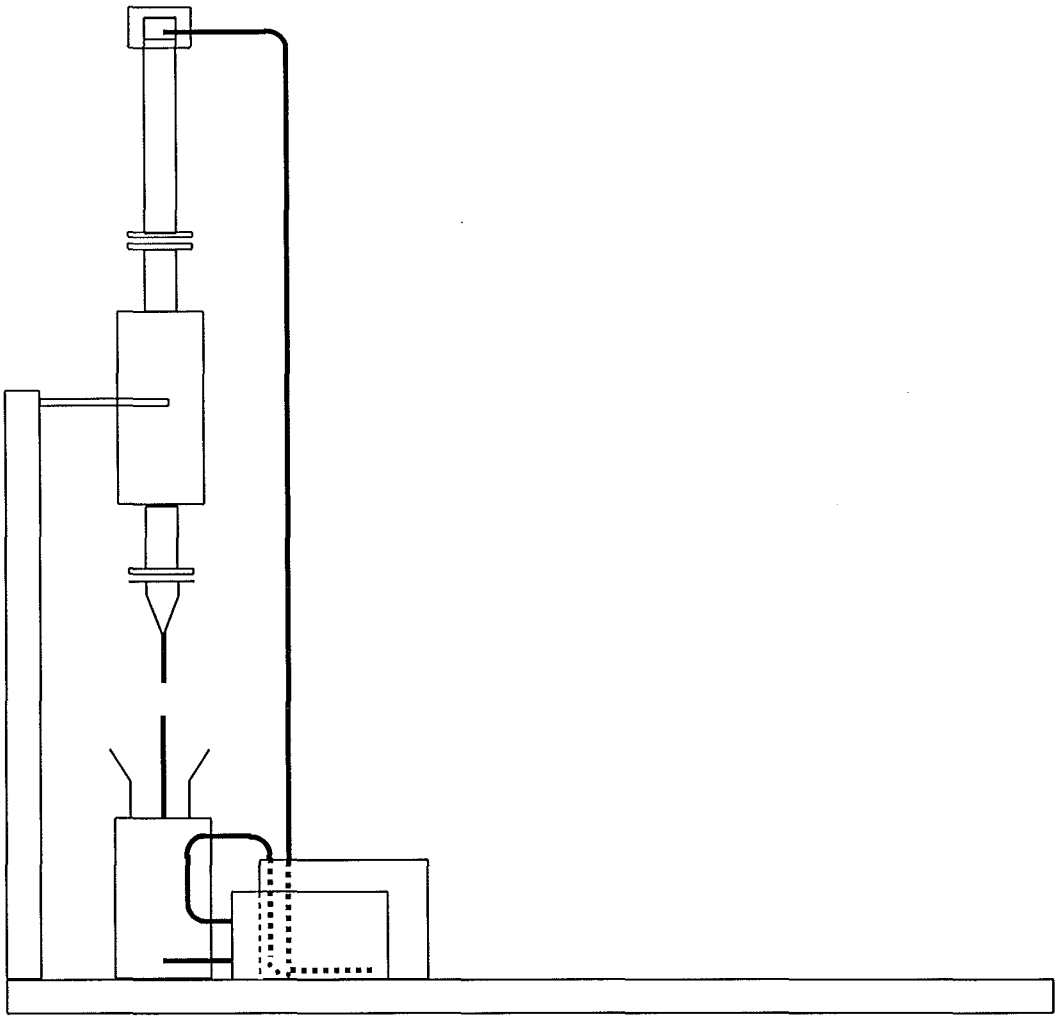


Figure B.1 *Schematic of apparatus*

'Product' Side

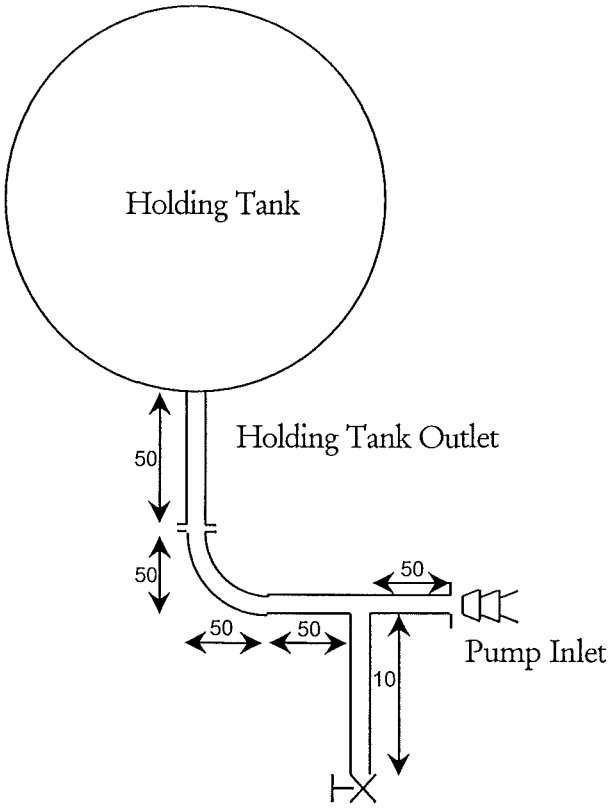


Plan View



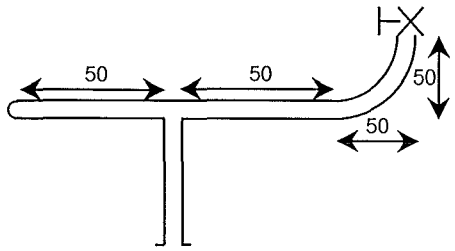
Side View

Figure B.2 *Plan and front elevation of product side*

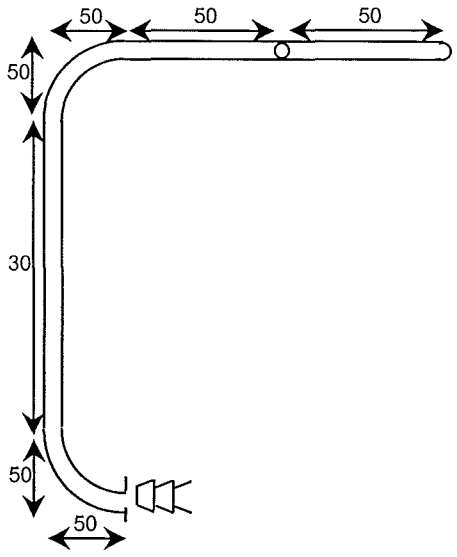


Plan View

Figure B.3 *Closeup of product side outlet*



Plan View



Side View

Figure B.4 *Plan and side elevation of pump outlet*

Appendix C - Pump Flow Rate Calculations

The flowrate for the lactose evaporators at startup is approximately 40,000 L/hr. The first effect of the Scheffiers has 676 tubes of 37mm internal diameter. The circumference of the heat transfer area is therefore:

Circumference = πd

Circumference = π x 0.037 m x 676

= 78.58m

For a standard startup:

Flow rate per meter = 40,000 L/hr x 1/60 minutes/hr x 1/78.58m

= 8.54 L/m min

Since the test plate has a flow area of width 40mm:

Flow rate = 0.04 m * 8.54 L/m min

= 0.340 L/min

(This is approximately setting 3.8 on the pump used in the experiment.)

Appendix D - Standard Operating Procedures

The apparatus consists of a test cell, which allows one side of a stainless steel plate to be heated by water, will the other is covered by a film of the fouling solution. The product is stored in a 5 L stainless steel catchpot until use. It is then passed through a water bath so that it reaches the test cell at the correct processing temperature.

1. Sand stainless steel test plate with P-600 sand paper. Wash carefully. Wait 24 hours for passivation to occur.
2. Turn on water bath stirrers and elements. Allow water baths to reach set points, which will take approximately two hours.
3. Weigh stainless steel test plate on 4dp (0.1 mg resolution) balance.
4. Place test plate in fouling block. Screw on nuts, being careful to tighten the eight nuts on either side of the test cell first. The four nuts at the top and bottom of the cell are to be finger tightened only.
5. Weigh out 1 L of permeate or make up fouling solution. (appendix E).
6. Pour fouling solution into catch pot.
7. Turn upper valve to 'bypass'.
8. Turn on product side pump.
9. If vacuum is required, open the main valve to the vacuum line until the desired point is passed. The open vacuum bleed valve until the set point is reached.
10. Circulate product until temperature in the catch pot reaches desired temperature.
11. If using unstable fluids such as calcium phosphate solutions, it may be best not to circulate before processing. This will avoid precipitation before reaching the fouling plate. In this situation the fluid can just be passed once through the heat exchanger. Turn upper valve to 'normal'.
12. Allow the flow over the test plate to stabilise, then adjust the flow spreader so that an even flow over the entire plate is obtained.
13. Turn on the 'steam side' pump and start timing.
14. Run for the desired time frame.
15. Turn off 'steam side' pump and stop timing.
16. Raise pressure to atmospheric if the apparatus has been running under vacuum.
17. Open catch pot valve. Open drain valve.

18. When the fluid has fully drained, turn on vacuum supply a small amount.
19. Rinse the catch pot with water.
20. When water coming out of drain valve is clear, close drain valve.
21. Refill the catch pot with water, then turn off vacuum supply.
22. Leaving catch pot valve open, turn on the product pump.
23. If flow over the test cell does not resume after ten seconds, open the drain valve slightly. This allows any air in the line to the product pump to escape.
24. Rinse the plate for five minutes.
25. Stop product pump, drain all water.
26. Disconnect steam side inlet and outlet to test cell. Carefully allowing water from the steam side to drain.
27. Undo ten nuts around test cell. Pull back of test cell off.
28. Take out test plate and place in oven at 105°C overnight.
29. Measure difference in plate weight.

Appendix E - Simulated Milk UltraFiltrate (SMUF)

As *tri*-Calcium phosphate has a solubility product of 1.20 x 10^{-29} mol/L (Gregory *et al*; 1974) at room temperature, a solution of $Ca_3(PO_4)_2$ can not be made just straight dissolution. The method suggested by Daufin *et al*, (1987), Jenness & Koops (1962) and its modified form (Wilson; 1997) was used.

It was suggested that to make a model whey permeate solution of the same ionic concentration as milk, the following recipe should be used.

1. 2.97 g/L $K_2HPO_4, 3H_2O$
2. 0.111 g/L $CaCl_2$
3. 2.85 mL/L 3N HCl
4. 2.95 g/L NaCl

The solutions should be mixed in the order 1, 3, 4, 2. This prevents any possible precipitation between solutions 1 and 2. Daufin (1987), reported that this method produces the similar ionic strengths (0.1) and pH (6.6) as those found in milk in whey.

Wilson (1997) suggested a similar method as set out below.

Add 50g each of KH_2PO_4 and $CaCl_2.H_2O$ into 380 mL tap water.

This produces a solution with 90 ppm equivalent $CaCO_3$ (same amount of Ca as 90 mg $CaCO_3$ in 1 L water.), and 922 ppm PO_4.

The method in this investigation used $CaCl_2.10H_2O$ and KH_2PO_4. All solutions were made to ½mol/L concentration of both components, but no pH correction was used. Solutions without acid adjustment of the pH were only slightly meta-stable, and if left at room temperature for around 30 minutes, started to precipitate. ¼ mol/L solutions at room temperature tended not to precipitate.

Appendix F - Calculation for Vapour Downcomers

These calculations are based on an evaporator processing 40,000 L/hr of whey permeate which enters the first effect at 85°C. The pressure in the first effect is assumed to be 43.9 kPa (78°C boiling point).

40,000 L/hr	=	11.1 L/s	= 10.8 kg/s	at 85°C
$h_{f,(85°C)}$	=	355.9 kJ/kg (Tucker, 1997)		
10.8 kg/s x 355.9 kJ/kg	=	3,844 kJ/s		

for the same flow rate at 80°C:

$h_{f,(80°C)}$	=	334.9 kJ/kg (Tucker, 1997)
10.8 kg/s * 334.9 kJ/kg	=	3,617 kJ/s

Therefore, 3,844 - 3,617 kJ/s = 227 kJ/s must be used to vaporise the liquid.

$\Delta h_{f,g(80°C)}$	=	2309 kJ/kg (Tucker, 1997)
227 kJ/s / 2309 kJ/kg	=	0.098 kg/s
	=	0.1 kg/s of vapour produced

checking with an energy balance

$h_{\text{fluid in evaporator at 85°C)}}$	=	$h_{\text{(fluid at 80°C)}} + h_{\text{(vapour at 80°C)}}$
$h_{\text{(fluid at 80°C)}}$	=	10.7 kg/s x 334.9 kJ/kg
	=	3,583 kJ/s
$h_{\text{(vapour at 80°C)}}$	=	0.1 kg/s x 2,644 kJ/kg
	=	264 kJ/s
3,844 kJ/s	=	3,583 kJ/s + 264 kJ/s
	=	3,847 kJ/s (correct to within 0.1%)

We wish to design vapour downcomers which remove this vapour at the rate it is created. A set of twelve downcomers could be build into an existing distribution plate very easily, and placed so that they empty into a region not directly over an evaporator tube. Designing for a vapour flow rate of 20 m/s:

$0.1\ kg/s * 3.407\ m^3/kg_{(at\ 47.4\ kPa)} = 0.341\ m^3/s$

$0.341\ m^3/s\ /\ 20\ m/s = 0.017\ m^2$

Dividing this area evenly into twelve tubes:

$0.017\ m^2\ /\ 12\ tubes = 1.42 * 10^{-3}\ m^2\ /\ tube$

$A = \pi r^2$

$r = 21.2\ mm$

say internal diameter of 51.0 mm or 2 inch.

Require 12 tubes of 51.0 mm I.D.

The pressure drop that occurs through the downcomers can be estimated as follows.

Wall friction may be estimated by equation F.1.:

$$\Delta P = \frac{4fL}{D}\rho\frac{v^2}{2} \qquad \text{F.1}$$

Where the fanning friction factor (f) may be assumed to be 0.004 (Perry & Green, 1984). The length was assumed to be 0.1 m.

$\Delta P = (4 \times 0.004 \times 0.1m\ /\ 0.0254m) \times 0.29\ kg/m \times (20^2\ m/s\ /\ 2)$

$= 1.8\ Pa$

$= \sim 0.18\ mmH_2O$

This can be considered negligible.

The losses in kinetic energy through the tube should also be considered. Assuming that the vapour flow loses all of its kinetic energy after passing through the downcomer and hitting the tube calandria.

$$\Delta P = \rho V^2/2$$
$$= 0.29\ kg/m^3 \times 20\ m/s / 2$$
$$= 58\ Pa$$
$$= \sim 6\ mm\ H_2O$$

The pressure drop through the distribution plate should be greater than the pressure drop through the downcomer. This can be checked.

Assume that the first effect of an evaporator contains a distribution plate with 1,640 holes of ϕ5mm, has a flow rate of 40,000 L/hr and an effect width of 1.580 m.

$$Q = C_d A\sqrt{2gh}$$

C_d is the coefficient of discharge and can assumed to be 0.6 (Streeter & Wylie, 1983). The flow rate through each hole can be calculated by assuming that the flow spreads itself evenly.

$$Q = (40\ m^3/hr \times 1/3{,}600\ seconds/hour) / 1{,}640\ holes$$
$$= 6.78 \times 10^{-6}\ m^3/s$$

$$A = \pi r^2$$
$$= \pi \times 0.0025^2$$
$$= 19.63 \times 10^{-6}\ m^2$$

Therefore:

$$6.78 \times 10^{-6}\ m^3/s = 0.6 \times 19.63 \times 10^{-6}\ m^2\ \sqrt{2 \times 9.81 m/s^2 \times h}$$
$$\Delta P = 0.0167 m\ H_2O$$
$$= \sim 17 mm\ H_2O$$

As this is more than the 6mm pressure drop through the downcomers, the vapour will not escape through the distribution plate.

Appendix G - Chemistry of the Orthophosphates

This information is summarised from Elliot (1994) and presented to combat the confusion caused by the erratic naming of calcium phosphates.

Octacalcium phosphate (OCP)

Synonyms: octacalcium bis(hydrogenphosphate tetrakis(phosphate) pentahydrate, tetracalcium hydrogen triphosphate trihydrate

Formula: $Ca_8(HPO_4)_2(PO_4).5H_2O$ - although water content is variable.

Discovered by Berzelius in 1836.

Kinetics and Growth:

OCP occurs as a transient intermediate in the precipitation of the thermodynamically more stable hydroxyapatite (HAP) because OCP nucleates and grows more easily than HAP. OCP and HAP have very similar structural chemistries. When OCP is first precipitated it may include many impurities, such as Mg^{2+} and Na^{+} ions, which are incorporated into the HAP when it forms. This process has been suggested as the reason for nonstoichiometric apatitic calcium phosphates.

The OCP unit cell is triclinic with cell constants a=19.692, b=9.523, c=6.835 Amstrons and α=90.15, β=92.54 and γ=108.65°. The asymmetric unit (the largest structural unit in which none of the atoms are related by symmetry) is $Ca_8(HPO_4)_2(PO_4).5H_2O$.

Dicalcium phosphate dihydrate (DCPD)

Synonyms: brushite, calcium monohydrogen phosphate dihydrate, dibasic calcium phosphate dihydrate, calcium hydrogen orthophosphate 2-hydrate

Formula: $CaHPO_4.2H_2O$

The mineral brushite was discovered in 1865 and named after American mineralogist G.J. Brush. DCPD can occur as an intermediate in the precipitation of HAP.

DCPD is monoclinic, with lattice parameters a=5.812$\pm$0.002, b=15.180$\pm$0.003, c=6.239$\pm$0.002 Angstroms and β=116°25$\pm$2.

Kinetics and Growth:

The growth of DCPD is proportional to the product $[Ca^{2+}][HPO_4^{2-}]$ over a wide range of Ca/P ratios which suggests a surface reaction controlled process. (Marshall & Nancollas; 1967). The rate is also proportional to the amount to be precipitated before equilibrium is reached.

Dicalcium phosphate anhydrous (DCPA)

Synonyms: anhydrous dicalcium, dicalcium phosphate, calcium hydrogen orthophosphate, monetite

Formula: $CaHPO_4$

Discovered as the mineral monetite in 1882 on the island of Moneta, in the West Indies.

DCPA has not been found in teeth or other bodily calcifications, despite the fact that it is more stable than DCPD in all conditions of temperature and pressure. This has been explained as being due to its very slow growth rate in comparison to DCPD. This difference may be due to hydrated ions becoming incorporated more easily into a hydrated crystal structure, or that the hydrated structure as a lower surface energy in the nucleation stage (Elliot, 1994).

At room temperature DCPD is triclinic.

Amorphous Calcium Phosphate (ACP)

Formula: N/A

ACP often occurs as a transient phase during the formation of calcium phosphates in aqueous systems, especially hydroxyapatites.

Appendix H - Economic Analysis of Additives

Tetrasodium pyrophosphate's effectiveness in reducing fouling was analysed. This section details the economic cost of such an additive and gives an example of how savings could be calculated.

Assuming that the cost of adding a dosing station to the existing process in minimal, only the running costs need to be considered. It was found that adding 0.1% by dry weight reduced fouling by two thirds. If this guarantees run unhindered run times of 14 hours, then the economic analysis becomes similar to that seen in appendix A.

Assuming that the evaporators run for 34 weeks a year (Styles, 1998):

34 weeks x 7 days x 24 hours = 5,710 hours / year

Untreated whey permeate:

7 hours processing + 2 hours cleaning = 2/7

Treated whey permeate:

14 hours processing + 2 hours cleaning = 2/14

Multiply the above fractions by 5,710 processing hours the amount of time spent on cleaning is found:

2/7 x 5,710 = 1,630 hours on cleaning

2/14 x 5,710 = 816 hours on cleaning

A clean uses about 70 L of 70% nitric acid per hour, which is diluted down to ~2%. At a cost of $1.30 / L (CCL, New Zealand).

Untreated: 114,100 L/year x $1.30 / L = $148,300

Treated: 57,100 L/year x $1.30 / L = $74,300

This is a CIP saving of **$74,000 /year**

Less time spent cleaning means more time processing product. The primary evaporation stage can sometimes be a bottleneck in the process and limit total production. If this is not the case, this section of the economics should be adjusted. Since the plant processes 40,000 L of 10% lactose per hour, each hour of extra processing time increases total production by:

40,000 L/hr x 10% lactose = 4 ton lactose /hour

After treatment:

1,630 - 816 = ~800 hours / year

800 extra hours will be available. Assuming that the marginal profit for a ton lactose is $100.

800 hours x 4 ton/hour x $100 /ton = $320,000

The increase in marginal profit: = **$320,000 / year**

The major running cost is the purchase of tetrasodium pyrophosphate For a flow rate of 40,000 L/hour

40,000 kg/hr * 12% total solids * 0.1% dosage rate = 4.8 kg/hour

At a price of $3.40 /kg (Hoogenboezem, 1998).

4.8 kg/hr * $3.40 /kg = $16.32 /hr

Over one year the cost will be:

$137,000

The total savings will be **$257,000 /year**

The additive costs $16.32 /hr, assuming that the whey permeate is 10% lactose

40,000 L/hour * 10% = 4 ton/hour

Therefore the extra cost will be **$16.32 /ton lactose**

Appendix I - X-ray Photoelectron Spectroscopy (XPS) Results

Three samples were analysed using an Kratos XSAM XPS device (University of Auckland, New Zealand). All samples were produced using the standard conditions of product temperature 60°C, 'steam' side temperature 75°C and a flow rate of 0.340 L/min (pump speed 3.8).

Table I.1 shows analysis of a sample fouled by untreated whey permeate. The values are in terms of elemental percentage.

Table I.1 *Elemental analysis of whey permeate fouling*

Sputter Time	0 min	2 min	5 min	10 min	Average
Ca	2.25	3.58	5.18	6.55	4.39
P	2.27	4.74	4.86	6.64	4.6275
K	0.41	0.31	0.15	0.48	0.3375
C	56.22	52.81	50.7	45.46	51.2975
O	30.71	29.96	29.42	33.22	30.8275
N	8.13	7.09	8.2	5.8	7.305
Na	0	1.51	1.47	1.84	1.205

The results in table I.2 were produced after whey permeate was heated to 80°C over two minutes.

Table I.2 *Elemental analysis of heat-treated whey permeate fouling*

Sputter Time	0 min	2 min	5 min	Average
Ca	2.21	3.86	5.59	3.88
P	2.23	3.87	6.35	4.15
K	0.38	0.37	0.28	0.34
C	57.58	56.53	50.9	55.0
O	32.83	30.28	30.46	31.19
N	4.76	3.7	4.59	4.35
Na	0	1.39	1.84	1.08

Table I.3 *Elemental analysis of heat-treated and centrifuged whey permeate fouling*

Sputter Time	0 min	2 min	5 min	10 min	Average
Ca	0	0	0	0.73	0.18
P	0	0.81	0.73	0.26	0.45
K	0.23	0.59	0.72	1.07	0.65
C	74.65	73.45	79.22	78.99	76.58
O	18.14	14.09	11.46	10.36	13.51
N	6.99	8.26	5.03	4.87	6.29
Na	0	1.48	1.59	2.17	1.75
Si	0	1.04	0	0	0.35
Cl	0	0.28	1.24	1.56	1.03